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Soil-plant water and its movement as determined by heavy water analysis

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SOIL-PLANT WATER AND ITS MOVEMENT AS DETERMINED BY HEAVY WATER ANALYSIS

by

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INTRODUCTION

A basic understanding of the movement of water in soils and plants has become increasingly important in past decades. This has been accentuated by the growing need for water, and especially so, when rainfall has been insufficient to satisfy the needs of mankind. Although many investigations of soil and plant water are found in the literature, many of these investigations do not go beyond the readily observable changes in plant and soil relationships commonly seen in nature. To obtain a better understanding of some basic principles in plant and soil water movement, techniques that are better and more refined than many currently used will have to be developed.

It is generally recognized that atomic isotopes are a valuable tool in both basic and applied research. Since the discovery of the hydrogen isotope, deuterium, many investigators, by utilizing this newly found form of hydrogen as a tracer, have been able to make valuable contributions to our basic knowledge of science. Nevertheless, it appears that in the field of soil and plant water movement and related fields, very little use has been made of deuterium as a tracer. This then suggests that an area of research remains open where deuterium can be applied in soils and soil-plant investigations.

This research problem was directed toward the use of

deuterium in a basic study of moisture diffusion in soils and of the processes of evaporation and transpiration. This field of research is listed by the Soil-Plant-Water Relations Committee of the Agricultural Board of the National Research Council, in its report of October, 1958, as one of the four most important fields needing study. In the research presented in this dissertation, deuterium in the form of DOH, and detected by the use of a mass spectrometer, was used to tag water, for following its movement in soils. The magnitude of this movement was characterized by values of self-diffusion coefficients. Deuterium enrichment equations were developed which are of value in calculating evaporation and transpiration under controlled laboratory conditions. The methodology is new in plant-soil-water studies and opens up new lines of investigation. The knowledge gained should give a better understanding of the physics involved in evaporation and transpiration and in soil moisture movement in general.

REVIEW OF LITERATURE

General

Much research work was done on deuterium after its discovery in 1932 by Urey, Murphy, and Brickwedde (42). Much of this work is summarized in a book by Kirshenbaum (21). Bibliographies, beginning in 1945, in research with deuterium (and tritium) have been issued by the National Bureau of Standards as found under Brown et al. (4) and Johnson et al. (19). In these bibliographies nearly 3,000 researches, many involving the use of deuterium as a tracer, are given. Most of this work consisted of the determination of the physical and chemical properties of deuterium. A large amount of biological work is also listed.

Many techniques for measuring deuterium have been developed. Books by Wilson et al. (50) and Kirshenbaum (21) give various methods of analysis of deuterium when in the form of deuterium hydroxide (DOH). Earlier methods of analysis were largely of the densimetric type. Later developed methods also were based upon the variation of some physical property of water as affected by its deuterium content. Still another method, employing a mass spectrometer, has been developed. The analysis of hydrogen isotopes by this method was worked out by Bleakney (2). The method has since been developed to high accuracy. All of the deuterium measurements reported in

this dissertation were obtained with a mass spectrometer.

Since deuterium is present in all natural water, it was of great interest to see if the deuterium concentration was relatively constant for various bodies and sources of water. Kirshenbaum (21) reported on the deuterium concentration of samples of natural water collected from numerous places on the North American Continent. The range of concentration encountered for different samples varied from 0.0139 mole percent to 0.0153 mole percent deuterium. Most of the samples tested measured 0.0148 mole percent deuterium. In all of the work reported herein the deuterium content of tap water was assumed to be 0.0150 mole percent deuterium. The mass spectrometer used is not accurate in the fourth decimal.

From the evidence obtained by determining the deuterium concentration of various bodies of water, it appeared that fractionation of the hydrogen isotopes is occurring in nature. Friedman and Redfield (15) found that during the freezing of water deuterium was concentrated in the ice phase. The enrichment in the ice phase ranged from 1.3 to 1.4 percent over that of the unfrozen water. In a laboratory experiment Washburn and Smith (48) obtained an isotopic fractionation of water by distillation. In another experiment these investigators obtained an isotopic fractionation of water by letting it be adsorbed by activated charcoal. In still another investigation Washburn and Smith (47) found that the water of

crystallization of borax tetrahydrate was enriched by 7 ppm. over that of normal water. Knop and Stern (22) showed that when water evaporated an equilibrium of the D concentration existed between the liquid water and the atmospheric water vapor. Under such conditions the remaining liquid always contained more of the heavier isotope than normal water. A literature review of isotope enrichment by fractionation as pertains to geological studies is given by Ingerson (18). Isotopic fractionation has also been observed in various physiological processes. These will be reviewed in the next section.

Tagged Water in Plant Research

The early agronomic investigations utilizing deuterium have been confined to tolerance levels exhibited by plants, plant seeds, and other biological systems. Caldwell and Doebbling (5) reported that germination of barley was virtually uninfluenced by deuterium concentration under 10 percent. Curry *et al.* (11) noted no difference in growth or respiration of wheat seedlings when grown in 0.46 mole percent D_2O. Similarly Melot (28) was unable to detect any difference in respiration rate of germinating seeds in 14.8, 38, and 94 mole percent D_2O during the first two days of respiration. On the other hand, Pratt and Curry (38) found that the growth of primary and secondary roots in wheat is greatly

retarded in D_2O solutions. Their results indicate that the growth rate in pure D_2O is 1/40th the value found in normal water. Using Nicotiana tabacum, Lewis (25) observed that while controls in normal water sprouted in 9 days, no macroscopic development was apparent in essentially pure D_2O. In 50-50 mixtures of normal and heavy water, development proceeded at about one-half the normal rate. In this connection Morowitz and Brown (29) recently reviewed 216 papers on the subject of deuterium tolerance levels and concluded that no harm was done to the physiological functions of the plant if the deuterium concentration was kept at very dilute concentrations. In the plant work reported herein the D_2O concentration was kept below 0.3 percent, a concentration which, based on the reported work, should not influence plant growth.

The observed fractionation of the hydrogen isotopes has been utilized in studying various physiological processes in plants or other organisms. Helvey (16) analyzed various components of honey and found D enrichments varying from 17 to 30 percent over that of water. Titani and Harada (41) observed enrichment of D in cane sugar (7.4 ppm.) and beet sugar (6.5 ppm.). Other carbohydrates averaged 6 ppm. Washburn and Smith (49) found that the sap of a willow tree was 2 percent richer in deuterium concentration and the wood had an enrichment increment double that of the sap. According to Washburn and Smith, since the vapor pressure of DOH is about 7 percent

below that of water at 25° C., it is possible that through transpiration, plants are acting as a still and that by fractional distillation of large quantities of water they will accumulate DOH in their tissue.

Cloud et al. (8) observed microbial fractionation of hydrogen isotopes in samples of bacterially generated gases. These gas samples were obtained from sediments found in the ocean. The analysis showed that deuterium was depleted by a factor of 20 over that of the ocean water.

Recently some work with deuterium was concerned with water movement in plant tissue. Ordin and Bonner (32) measured the permeability of Avena (oat) coleoptile sections to water. This was accomplished by measuring the rate of diffusion of the DOH into the coleoptile sections. Their results indicate that the turgor of the tissue had no influence on water permeability, and the cell wall was the primary limitation for faster water movement. With a similar technique Ordin and Kramer (33) measured the permeability of Vicia faba (horse bean) root segments to water. The results from this experiment indicate that the cytoplasm rather than the cell walls constitutes the principal resistance to water movement in the root segments. Reviewing the work of these two experiments Bonner (3) showed that Fick's Second Law, rather than his First Law, is applicable when water diffuses from free water into plant tissue. He stated that the problem of

water movement in plants is becoming increasingly amenable to mathematical analysis and emphasized the need of further basic research.

In a similar study Kutyurin (24) found that a mobile equilibrium exists between the content of heavy water in the cellular water and in the water of the surrounding medium. Furthermore this relationship is independent of the light influence. He also found that the rate of DOH penetration into the cells and the equilibrium concentration is a function of temperature and is independent of the deuterium concentration. This is in general agreement with Bonner's (3) study.

Recently Polyakow and Germogenova (37) found that the D concentration in plants, growing in soils containing tagged water, was a function of the soil moisture content. The maximum water entering a growing plant as determined from the D concentration in the plant was found at 68 percent of the field capacity. In another experiment by the same investigators the water taken up by plants as determined from the D concentration in the plant was dependent upon the sodium chloride concentration in the solution culture. The water uptake was represented by a parabola when plotted as a function of the sodium chloride concentration. The minimum value of water uptake occurred at a concentration of 1.5-3.0 percent sodium chloride. This reported value of 1.5-3.0 percent appears to the writer to be contradictory to some generally

accepted soil-water-plant concepts.

Tagged Water in Soil Research

Several investigations involving heavy water have been conducted in soils research. McAuliffe et al. (27) measured the extent of hydroxylic surfaces for kaolinite, halloysite, diaspore, and gibbsite by the amount of exchange that occurred between D and H. These investigators also showed that the rate of these exchange reactions is a function of the temperature. Faucher and Thomas (14) in a similar experiment with montmorillonite found that the exchange of D for H is very rapid for 75 percent of the total water associated with the clay mineral and that very little further exchange occurs even after contact periods of 120 hours. Romo (39) observed the actual presence of deuterium in the clay lattice from infrared measurements. He concluded that the rate of exchange appears to be characterized by two steps: one in which the exchange takes place predominantly on the surface hydroxyls, and the other one in which a process of diffusion takes place to affect exchange of the intralattice hydroxyls.

Recently Kaufman and Orlob (20) made an evaluation of tritium as a ground water tracer. Although tritiated water has slightly different properties than deuteriated water, the same basic principles apply. They concluded that exchanges with soil-bound water may reduce the velocity of the tracer

front to the extent of about 5 percent. Similar conclusions were drawn in a series of ground-water studies involving tritium by Von Buttlar and Wendt (43).

Self-Diffusion of Water

Methods for studying self-diffusion of water have become more practicable with availability of hydrogen isotopes. Self-diffusion is defined by Crank (10, p. 228) as a measure of the true mobility of labeled molecules with respect to the stationary solution. Recently in a series of papers Wang (44, 45) and Wang et al. (46), using an experimental method developed by Stefan (40), measured self-diffusion coefficients of liquid water at various temperatures in an effort to verify the semi-crystalline (Crafts et al. (9, p. 15)) structure of water. By using $H^1H^2O^{16}$ as a tracer, the self-diffusion coefficient of water at 25° C. was found to be 2.34 x 10^{-5} cm.^{2}/sec. By using tracer forms involving tritium and oxygen, $H^1H^3O^{16}$ and $H^1H^1O^{18}$, respectively, the magnitude of the self-diffusion coefficient was found to change very little. A conclusion drawn from the latter aspect of this study was that the movement of hydrogen isotope atoms in a water medium occurs primarily in the form of water molecules and not as successive exchanges of hydrogen isotope atoms between neighboring water molecules. This conclusion indicates that the process of self-diffusion in water is carried out essentially

by single water molecules that are in thermal equilibrium with the surrounding semi-crystalline water lattice.

Because of the limited amount of research that has been done in which deuterium is applied to soils and to soil-plant investigations, as is clear from above, an area for more basic and applied research remains open.

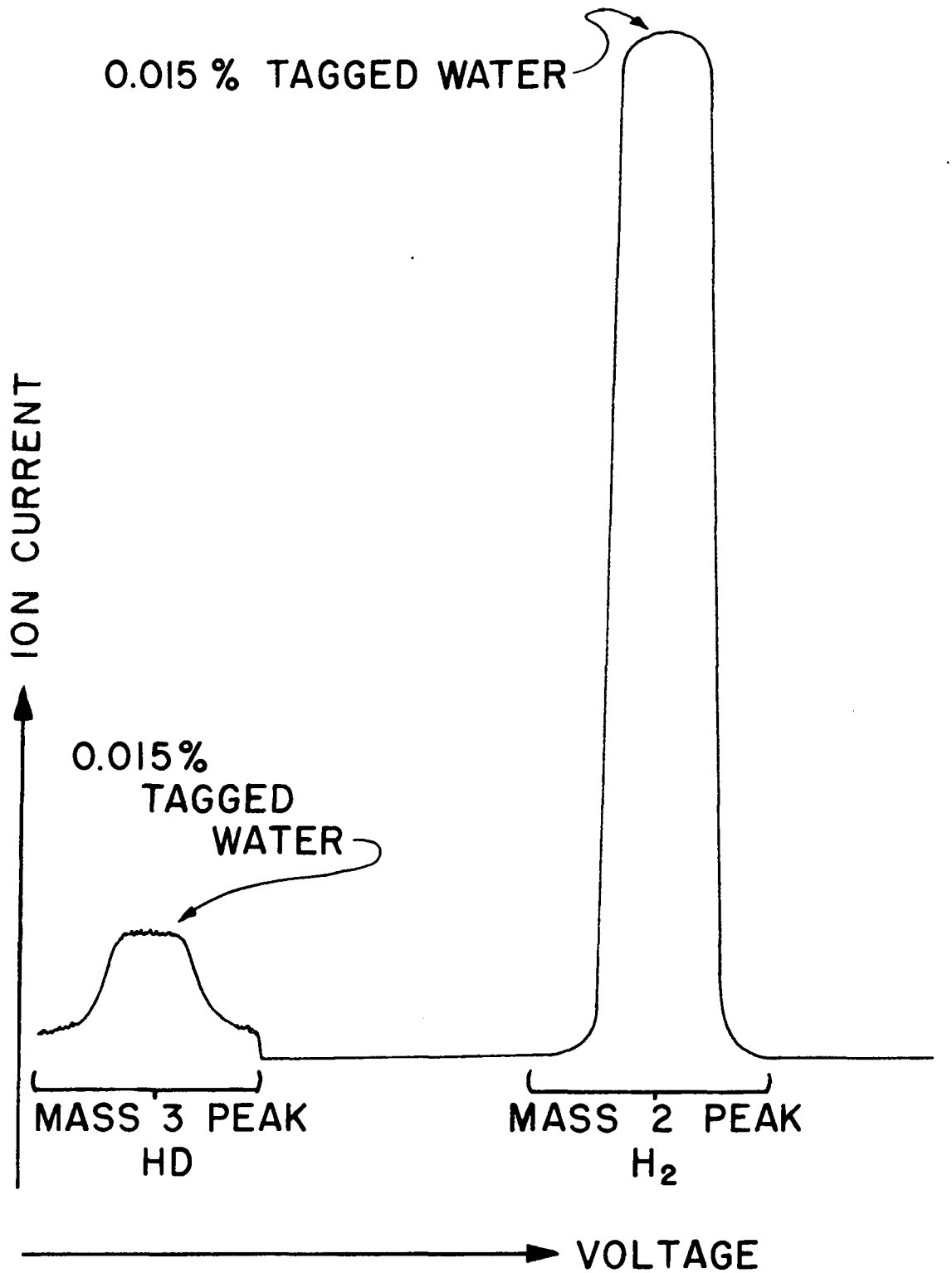
TECHNIQUE FOR MEASURING DEUTERIUM

General Description of Apparatus and Technique

The technique for the experiments that follow is built around the use of a model 21-620 mass spectrometer obtained from the Consolidated Electrodynamics Corporation. This mass spectrometer is a variable voltage (as opposed to a variable magnetic field) device. As the voltage is varied, it brings ionized molecules or atoms of different masses from a sample being analyzed into focus on a collector plate. The lower voltages bring the higher masses into focus and the higher voltages, the lower masses. The ionized molecules or atoms, when they strike the plate, comprise an electric current which is amplified and automatically plotted, versus voltage, by the instrument. Each ion type comes into focus for a certain voltage and causes a peak in the plot of ion current versus voltage. The height of the peak depends on the number of molecules or atoms of the type corresponding to the voltage of that peak in the sample being analyzed. Typical mass 2 and mass 3 peaks are shown in Figure 1.

This instrument was obtained for an agronomic research program of wide interest, especially for studies utilizing isotopes of hydrogen, nitrogen, and oxygen. The instrument, in order to cover a wide range of interest, sacrifices sensitivity in detecting isotopes of any one atom type. Neverthe-

Figure 1. Mass 2 and mass 3 peaks obtained with the mass spectometer from a mixture of 0.015 percent tagged water (normal water)


0.015 % TAGGED WATER
ION CURRENT
0.015%
TAGGED
WATER
MASS 3 PEAK
HD
MASS 2 PEAK
H_2
VOLTAGE

less by developing careful techniques with the instrument small differences in molar concentrations of deuterium could be measured. These differences were in the range of ± 5 parts per million compared with ± 1 part per million obtainable with a more specialized mass spectrometer. Here the molar concentration, C, is defined by the equation

$$C = N_D/(N_D + N_H) \qquad (1)$$

where

N_D = moles of D_2O

N_H = moles of H_2O

The techniques that were developed are based in part on procedures described in Kirshenbaum (21, especially pp. 109-150) and in Wilson et al. (50). In general, the procedure of sample analysis consists of comparing the ratio resulting from the peak height readings (Figure 1) of DH and H_2 molecules of the standard with the corresponding ratio of the unknowns. The peaks due to H_2 (from H_2O) are called mass 2 peaks; those of DH (from DOH) are called mass 3 peaks. The height of a peak depends on the sensitivity setting of the attenuator of the instrument, as well as upon the concentration. The two peaks shown in Figure 1 were obtained at different sensitivities.

Preparation of Standards

The heavy water which was used in preparing the standards and also in tagging samples was 99.5 percent pure D_2O obtained from the Stuart Oxygen Company. The cost was approximately $0.40 per gram. The normal water that was used was ordinary tap water which had been run through a resin column to remove minerals and other impurities. High quality distilled water could also have been used.

A portion of the 99.5 percent pure D_2O was mixed with a portion of normal H_2O and the resulting concentration was determined by utilizing equation 1 in a modified form requiring some new notations. These notations are now introduced. The 99.5 percent pure D_2O is referred to as type 1 material and designated by subscript "1" to refer to quantities associated with it; likewise the normal water is designated as type 2 material and subscript "2" is used to refer to quantities associated with it.

Let

W_1 = weight of the quantity of type 1 water (determined by weighing).

F_1 = weight fraction of the D_2O in type 1 water (= 0.995, known from supplier).

$1 - F_1$ = weight fraction of H_2O in type 1 water (= 1 - 0.995 = 0.005, determined from known value of F_1).

W_2 = weight of the quantity of the type 2 water (determined by weighing).

F_2 = weight fraction of the D_2O in the type 2 water (= 0.00015, a figure given by Kirshenbaum (21, p. 396)).

$1 - F_2$ = weight fraction of H_2O in type 2 water (= 1 - 0.00015 = 0.99985, determined from known value of F_2).

M_D = the molecular weight of pure D_2O (= 20.03 grams per mole, from Kirshenbaum (21, p. 15)).

M_H = the molecular weight of pure H_2O (= 18.02 grams per mole, from any chemistry handbook).

From the above definitions it is seen that for determining N_D and N_H in equation 1

$$N_D = (W_1F_1 + W_2F_2)/M_D \qquad (2)$$

$$N_H = (1 - F_1)W_1 + (1 - F_2)W_2/M_H \qquad (3)$$

The weighings of W_1 and W_2 could be and were when necessary, carried out to the nearest 0.1 milligram. A set of sample values for substitution in the above equation, and which also indicates amounts of materials involved, is the following: W_1 = 0.2976 gram, F_1 = 0.995, W_2 = 99.63 grams, F_2 = 0.00015, M_D = 20.03 grams per mole and M_H = 18.02 grams per mole. From these values, N_D = 0.01553, N_H = 5.5294 and, using equation 1,

$$C = 0.01553/(0.01553 + 5.5294) = 0.002800$$

That is, the percentage molar concentration is

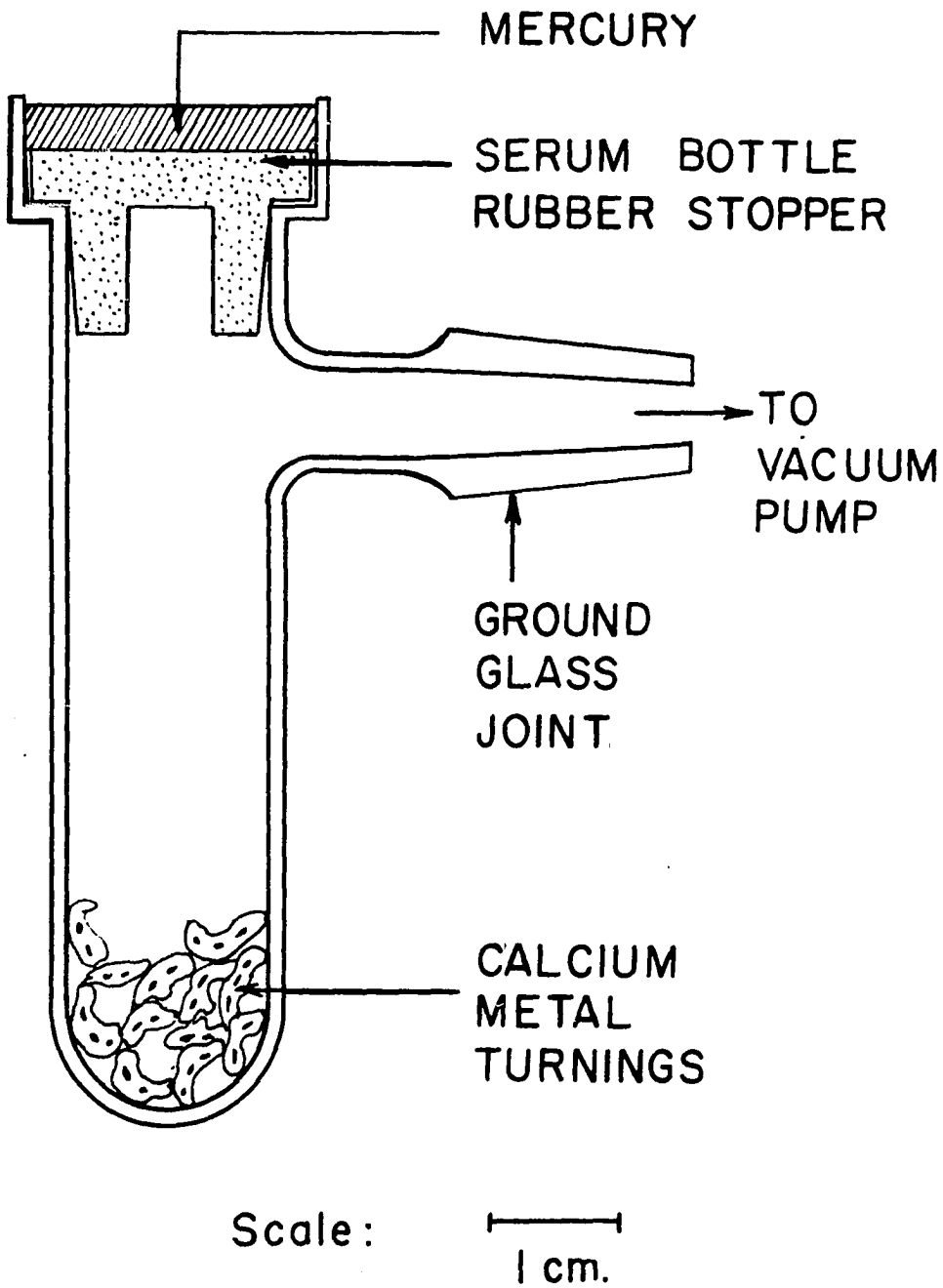
$$C = 0.002800 \times 100 = 0.2800 \text{ percent} \qquad (4)$$

The concentration of equation 4 is one of the concentrations used for a standard. Several standard concentrations were needed. The standards were prepared to be of approximately the same concentrations as those of the unknown samples. In some cases the standard concentrations were much less than those shown in equation 4 but never less than that of normal water (0.00015 = 0.015 percent D). In equations 1 and 4 if the numerator and denominator on the right side are multiplied by Avogodro's number, then the right side of the equation gives the ratio of D atoms to (D + H) atoms; that is the equations, as they stand, besides giving the molar concentration, also give the atom concentration.

Breakdown of Standards

One of the limitations of making an analysis of DOH water with a mass spectrometer is the necessity of converting water to hydrogen gas before the analysis can be made. The technique presently used is to react water with calcium metal to obtain H_2, HD, and calcium hydroxide. This can be done rather rapidly with a gas synthesis apparatus as described by Kirshenbaum (21) or with one described by Wilson et al. (50). The latter has been described for nitrogen isotope analysis. It was, for the present work, modified (Figure 2) for hydrogen isotope analysis. The reactor vial shown in the figure was

Figure 2. Reactor vial for preparing H_2 and DH gases from tagged water samples


MERCURY
SERUM BOTTLE
RUBBER STOPPER
TO
VACUUM
PUMP
GROUND
GLASS
JOINT
CALCIUM
METAL
TURNINGS
Scale:
1 cm.

the principal item modified. The reactor vial was used for breaking down the water sample into its component hydrogen isotope gases. A small water sample (0.2 - 0.6 cc.) was introduced into the reactor vial by means of a small hypodermic syringe, which was pierced through the serum bottle rubber stopper shown in Figure 2. The syringe needle passed through the stopper and into the reactor vial previously evacuated, and containing about one gram of calcium metal turnings. When the water struck the calcium metal, the water reacted with the calcium according to

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow \qquad (5)$$

$$Ca + 2DOH \longrightarrow Ca\begin{matrix}OH\\OD\end{matrix} + HD\uparrow \qquad (6)$$

In equations 5 and 6 some of the H and some of the D remained with the calcium when the reactants formed calcium hydroxide. This did not matter since the proportion of O and H remaining with the calcium would be the same for the standard and the unknown samples. To assure that no leakage occurred around the syringe needle or around the edges of the serum bottle rubber stopper, a layer of mercury was placed over the stopper as shown in Figure 2.

The hydrogen gases upon completion of the reactions, shown in equations 5 and 6, were pumped by means of a mercury pump into a small gas container, not shown in Figure 2, having a ground glass joint and a stopcock. This glass container was then connected by means of the ground glass joint to the

inlet system of the mass spectrometer whenever a standard of this specified concentration was to be run.

Analysis of Standards with the Mass Spectrometer

Three sets of mass 2 and mass 3 measurements were usually taken per sample. The ratio of the mass 3 peak height to the mass 2 peak height was calculated for each set. These ratios generally decreased with the concentration of the gases, that is, gas pressure. To be able to compare ratios of standards and unknowns it was necessary to adjust the ratio to some arbitrary pressure. However, rather than measure pressure, which was of the order of 1 mm. Hg, it was found more convenient to use the mass 2 peak height as an index of pressure. A regression coefficient could be calculated from mass 3/mass 2 ratios and the mass 2 peak heights. The mass 3/mass 2 ratio could then be corrected to some pre-selected pressure or mass 2 peak height. This adjustment was much more critical at small D values (0.0150 percent as compared to 0.3 percent). By plotting the calculated mass 3/mass 2 ratio versus the known atom percent D (as determined by the described gravimetric method, equations 2, 3, and 4) of seven standards, a very good linear relationship was obtained, the correlation coefficient r being 0.99995.

Comparison of Standards with Unknowns

The procedure described for the breakdown and analysis of the standard samples was the same as that used for samples of unknown D concentration. After obtaining the mass 3/mass 2 ratio for the unknowns, the curve for the standard samples was then utilized in determining the D concentration of the unknowns. Although a high degree of precision could be obtained when running the same samples repeatedly over a short period of time, the measurements were not highly reproducible after a period of several days or a week. Thus a permanently established calibration curve, as mentioned above, could not be used.

With the present technique, two widely separated calibration points were run intermittently with a number of unknowns. These points generally represented the lower and upper limits of the D concentration used. The unknowns and the standards were usually run in ascending or descending order of concentration. This reduced the memory effect of the instrument. With this technique standard deviations were, for low concentrations (say 0.015 percent), as small as $\pm$ 0.0005 percent or less, that is $\pm$ 5 parts in 150 parts of D. The standard deviations went as high as $\pm$ 0.003 percent for the high D concentrations (say 0.300 percent), that is $\pm$ 1 part per 100 parts of D.

PLANT EXPERIMENTS

Purpose of Experiments

The root environment of growing plants as affected by the physical properties of the soil has a pronounced effect upon the total quantity of water transpired. The effect of oxygen and carbon dioxide concentrations in the root zone upon the uptake of water by plants was shown by Chang and Loomis (6), Kramer (23), and other investigators in culture solution work. Similarly, the absorption of water by plants is affected by soil temperature. Investigations by Clements and Martin (7), Arndt (1), Nelson (30), and others have shown that the water absorption by plants is affected by different soil temperatures. Still in other areas, such as moisture tension and osmotic stress of soil-plant work, the quantity of water absorbed is closely related to the energy level at which the water is held by soil or the electrolyte.

Although a voluminous amount of work has been done in these areas and much has been learned by growing plants under these environments, yet the fact remains that under field conditions plant roots frequently may be exposed to a whole range of these environmental conditions at one time. Comparatively very little is known how roots of one plant respond when exposed to different root environments simultaneously.

The purpose of this experiment is to evaluate, using a

split-root technique and DOH, how water usage is influenced by physical factors of the root zone. This technique requires that half of the plant roots be grown in one environment, say at the left side of a dividing barrier, and the other half be grown on the right side of the same barrier. The environments of the two sides can be varied. This technique is unlike that commonly employed in studying the effects of physical conditions on plant growth in that the whole root system of one plant is not exposed to one root environment. Use of a split-root technique is not new. Recently Eaton (13) used the split-root method successfully in calculating the overall tension in the plant xylem. Tagged water has apparently not previously been used in split-root studies.

In this study the technique consisted of tagging the soil moisture with DOH on one side of a root barrier and leaving the other side untagged. The environment of the two sides was varied so that different rates of water absorption could be anticipated. The uptake of water from either side was calculated from the deuterium concentration found in the leaves and from the total moisture lost.

Before any realistic attempt could be made in this type of study, information was needed on the rate of heavy water enrichment which resulted from the water transpiring from the leaves. Because the vapor pressure of DOH is approximately 7 percent less than that of normal water at 25° C. (Kirshen-

baum (21, p. 25)), there is a natural tendency of the untagged molecules to evaporate faster than the tagged molecules and thereby bring about an enrichment of the remaining water. It has been noted that deuterium concentrations found in honey, ice, and willow trees as reported by Helvey (16), Friedman and Redfield (15), and Washburn and Smith (49), respectively, were higher than those found in normal water. Vapor pressure differences, preferential chemical or physical binding, slower diffusion rates, and other different physical properties of heavy water were reasons given by the investigators for these observations. Since the D content of the leaf water was to be used in determining the source of the water, the enrichment effect and the magnitude of the error that this factor might introduce in the deuterium determinations had to be elucidated before the primary objective could be pursued further. It was also of special interest to know how much enrichment had occurred after known quantities of water (DOH-HOH) had evaporated from the leaves.

Deuterium Enrichment of Water

Theoretical considerations

Assumptions and definitions The problem was found to be amenable to mathematical analysis when a model was used which was based upon the satisfying of certain specific experimental conditions. Two theoretical deuterium enrichment

equations were derived. Case 1 applies when the volume of the water system does not remain constant, and Case 2 applies when the volume of the water system remains constant. The water system may be defined as any body of water from which water is evaporating. In either case the objective was to find a relationship between the amount evaporated and the degree of enrichment for the remaining water. For either of the equations to be valid the following assumptions were made:

I. The water system must be isolated from normal atmospheric water vapor.

II. The temperature must remain constant.

III. The liquid as it vaporizes must be removed from the system.

IV. The deuterium content of the water system in question must be homogeneous.

Symbols and their notation for the derivation of the deuterium enrichment equations are given as follows:

$\bar{p}_{DOH}$ = vapor pressure of DOH

$\bar{p}_{HOH}$ = vapor pressure of HOH

p_{DOH} = partial vapor pressure of DOH

p_{HOH} = partial vapor pressure of HOH

p_t = total vapor pressure of the liquid components

Q = quantity of water evaporated

V = volume of the water system

z = mole fraction of DOH in water added

x_o = mole fraction of DOH in liquid system initially

x = mole fraction of DOH in liquid system after an amount Q has evaporated

y = mole fraction of DOH in the vapor phase at any time

$a = \bar{P}_{DOH}/\bar{P}_{HOH}$

ln = logarithm to base e (= 2.718)

Case 1 If one assumes that from a water system of known volume and known deuterium concentration each incremental volume of water that is evaporated is removed from the system so that it does not return to the liquid from the vapor phase, then it is possible to calculate the exact deuterium concentration of the water in the system from a derived equation. Examples of this in agronomic research might be the evaporation of water from an isolated small body of water, from an isolated volume of wet soil, or a turgid plant leaf or cell that has been isolated from its water source. With the examples cited the assumptions that were previously given are not satisfied; therefore, an evaporating water system was constructed in the laboratory that would fulfill the conditions. The validity of the equations was checked with the laboratory experimental data. Further generalities were then applied to various water systems found in nature.

To derive the needed differential equation use was made of Raoult's law of partial vapor pressure and of Dalton's law of partial pressure. Raoult's law states that the partial

vapor pressure of any volatile constituent of a solution is equal to the vapor pressure of the pure constituent multiplied by the molar fraction of that constituent in solution. Thus one obtains

$$p_{DOH} = \bar{p}_{DOH}(x) \tag{7}$$

Since the total vapor pressure is equal to the sum of the components, it may be seen that

$$p_t = p_{DOH} + p_{HOH} \tag{8}$$

or

$$p_t = \bar{p}_{DOH}(x) + \bar{p}_{HOH}(1 - x)$$

Returning to equation 7 and dividing each side by p_t, one obtains

$$p_{DOH}/p_t = \bar{p}_{DOH}(x)/p_t \tag{9}$$

By combining equations 8 and 9 and letting p_{DOH}/p_t equal y, the mole fraction of deuterium in the vapor phase is found to be

$$y = \frac{\bar{p}_{DOH}(x)}{\bar{p}_{DOH}(x) + \bar{p}_{HOH}(1 - x)} \tag{10}$$

Dividing the numerator and denominator on the right hand side of equation 10 by $\bar{p}_{HOH}$ and using the definition of a, one finds

$$y = ax/(1 - x + ax) \tag{11}$$

where y, the mole fraction of the vapor phase, is now a function of the mole fraction of the liquid phase.

We now proceed to the derivation of the differential equation proper.

In deriving the differential equation, if one assumes that from a unit mass of mixture of DOH and HOH Q volume-units of water have evaporated and if one further assumes that the deuterium concentration of the water evaporated is y, then approximately Qy units of DOH will have been evaporated and (1 - Q) volume-units of water and (1 - Q)x units of DOH will remain. Now, if one further assumes that a small additional increment of dQ units of the mixture evaporates, then the amount of DOH in the vapor form of these dQ units of mixture will be ydQ and the change in DOH content in the liquid water will be $d\left[(1 - Q)x\right]$. Thus the change in the total units of DOH in the remaining liquid is equal to that increment which has evaporated. This is expressed by the differential equation

$$-d\left[(1 - Q)x\right] = ydQ \qquad (12)$$

The objective is to find a relation between Q, y, and x which makes (12) valid. Upon differentiating the left-hand side, one obtains

$$-(1 - Q)dx + xdQ = ydQ \qquad (13)$$

Combining 13 with 11, it is seen that

$$-(1 - Q)dx = \left(\frac{ax}{1 - x + ax} - x\right)dQ$$

Separating variables and integrating from Q = 0 to Q and from $x = x_o$ to x, one obtains

$$\ln (1 - Q) = -\left[\left(\frac{a}{a - 1}\right) \ln \left(\frac{1 - x}{1 - x_o}\right) + \left(\frac{1}{a - 1}\right) \ln \left(\frac{x_o}{x}\right)\right] \quad (14)$$

where $1 > x > x_o$. The values, a and x_o, are experimentally determined and values of x are arbitrarily chosen to obtain a corresponding value of Q in equation 14. Thus one obtains the general relationship

$$Q = f(x)$$

By plotting values of Q as a function of x, it is possible to determine x by measuring only the quantity of water evaporated. The difference between x and x_o is the enrichment value that is needed.

Case 2 Agronomic examples that may approach the evaporation from a constant volume system in agronomic research are that of a slowly transpiring leaf, an evaporating soil surface overlying a water table of constant height, and an infinitely large body of water. Again the assumptions are not fulfilled in these examples and an imaginary model, which fulfills these conditions, is used to permit a mathematical analysis.

If one assumes that a quantity, dQ, of water evaporates from a DOH-HOH system, the loss in deuterium content will be ydQ. Since water is replaced as it is lost, the gain in water content will be dQ and the gain in deuterium content will be zdQ. The difference between gain and loss of water content is

zero but the difference between gain and loss of deuterium content is Vdx. When $z > y$, the differential equation is of the form

$$Vdx = (z - y)dQ \tag{15}$$

Substituting 11 into 15, one finds

$$Vdx = \left(z - \frac{ax}{1 - x + ax}\right)dQ$$

and simplifying

$$dQ = V\left(\frac{1 - x + ax}{z - zx + azx - ax}\right)dx$$

Further simplifying of the left-hand side gives

$$dQ = V\left[\frac{x + \frac{1}{a - 1}}{\left(z - \frac{a}{a - 1}\right)x + \frac{z}{a - 1}}\right]dx \tag{16}$$

Now defining A, B, and C by

$$\frac{1}{a - 1} = A \tag{17a}$$

$$z - \frac{a}{a - 1} = B \tag{17b}$$

$$\frac{z}{a - 1} = C \tag{17c}$$

one obtains upon substituting into equation 16 the result

$$dQ = V\left(\frac{x + A}{Bx + C}\right)dx$$

By dividing $(Bx + C)$ into $(x + A)$ to obtain an improper fractions, it is found that

$$dQ = V\left[\frac{1}{B} + \frac{(A - C/B)}{(C + Bx)}\right]dx$$

Integration of x from x_o to x and Q from 0 to Q gives

$$Q = V\left\{ \frac{x - x_o}{B} + \left[\frac{(A - C)/B}{B}\right] \ln \left[\frac{(C + Bx)}{(C + Bx_o)}\right]\right\} \qquad (18)$$

Now substituting 17a, 17b, and 17c into 18 and simplifying, one sees that

$$Q = V\left(\frac{x - x_o}{z - \frac{a}{a - 1}} - \left\{\frac{a}{\left[z(a - 1) - a\right]^2}\right\} \ln \left\{\frac{z + \left[z(a - 1) - a\right]x}{z + \left[z(a - 1) - a\right]x_o}\right\}\right) \qquad (19)$$

In equation 17 the quantities a, z, x_o, and V are again experimentally determined constants and x is arbitrarily chosen to obtain a corresponding value of Q in equation 19. Then, as in equation 14, the function reduces to

$$Q = f(x)$$

The limits of the arbitrarily chosen values of x may be determined by letting Q = 0 and ∞. At Q = 0, we have $x = x_o$. At $Q = \infty$ the numerator of the ln term becomes zero and we have

$$x = \frac{-z}{z(a - 1) - a}$$

Since z(a - 1) is negligible compared to a, the former term may be discarded and the upper limit of x is, as it should be, z/a. Thus values of x are limited to the interval, $x_o < x < z/a$.

When $z < y$, equation 15 takes the same form preceded by a negative sign. Now $x < x_o$ and the ln term of equation 19 takes on a positive sign (ratio becomes greater than 1) and

the resulting Q is again positive.

Equation 14, although pertaining to a system of reducing volume, may be used to get the constant volume result given by equation 19. To use equation 14 for the latter case it is necessary to keep a continuous running account of the DOH concentrations in successively calculated remaining liquid systems and also to keep a running account of the quantity of water added along with its DOH concentration. Thus when using equation 14, a new DOH concentration must be calculated after each loss and addition of water. This is not necessary when using equation 19. A plot of an example calculation will be shown in "Results" to demonstrate this relationship between the two enrichment equations. The calculation shows that the same result is obtained from both equations and that they therefore appear both correct in describing the physical situation.

Method of testing theory

To see if experimental data would coincide with that given by the theoretical equations, an experiment was conducted whereby the assumptions given previously were largely fulfilled. For the sake of brevity only the case of equation 14 was checked experimentally. The enrichment phenomenon in either case is physically the same, and thus experimental proof for one case will satisfy. In checking the fit between

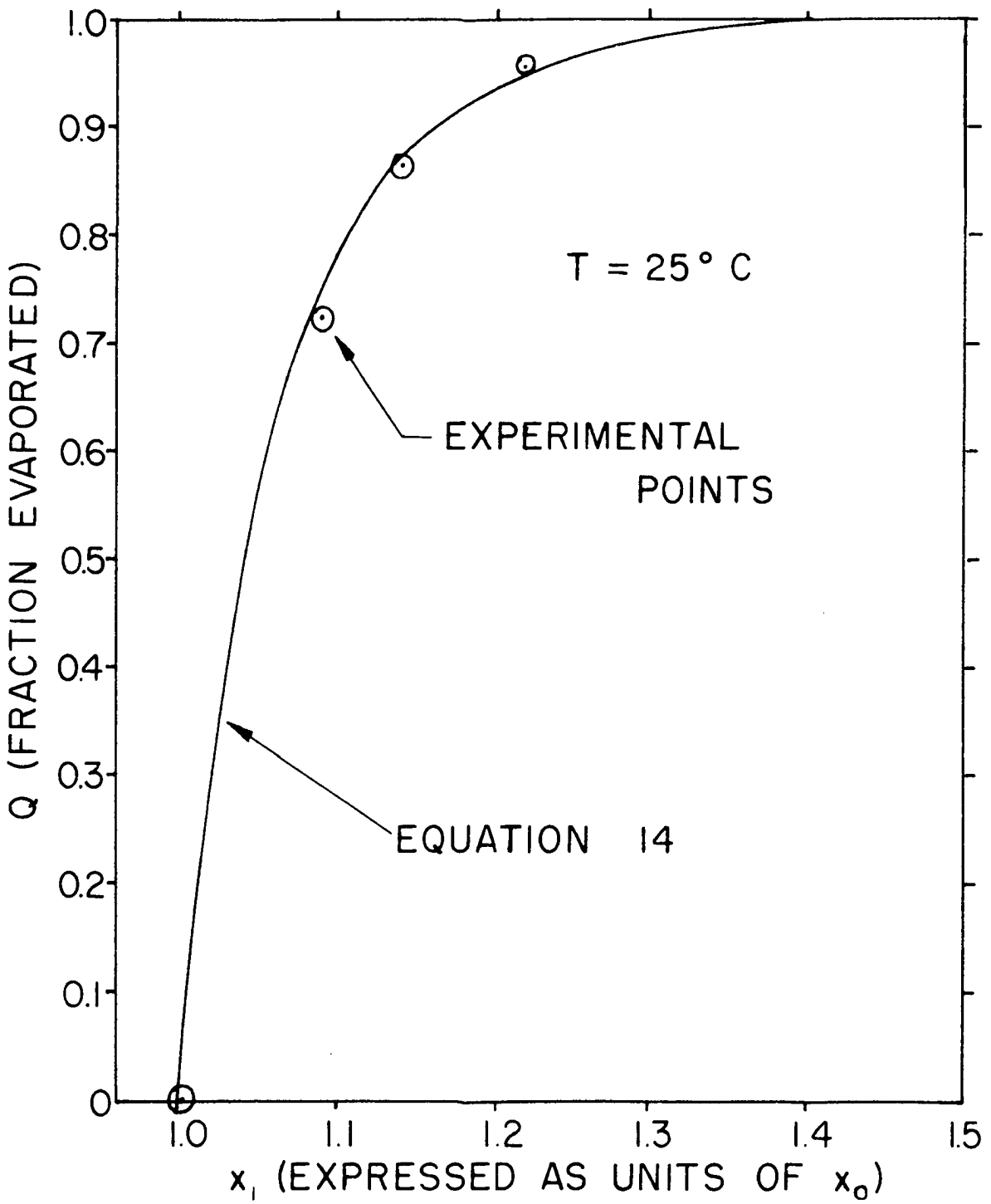
experiment and theory Case 1 was chosen over Case 2 because Case 1 presents fewer experimental problems; however, checking Case 2 is certainly not out of the realm of possibility.

For checking Case 1, 50 cc. of tagged water were placed in a Petri dish, which in turn was placed in a desiccator. A dehydrant, anhydrous magnesium perchlorate, was also placed in the desiccator near the water. By placing the lid on the desiccator and thereby excluding atmospheric water vapor, condition I was fulfilled; by placing the desiccator and its contents in a constant temperature environment, condition II was fulfilled; and by placing the dehydrant in the system and thereby removing the water vapor from the system, condition III was fulfilled. The dehydrant was changed several times during the experiment. There was some question about the fourth assumption, that is, the homogeneity of the water system, since the water was not stirred during the experiment. The homogeneity problem was largely overcome by the relatively shallow layer of water in the Petri dish; however a magnetic stirrer or some device for stirring the remaining liquid probably would have been advantageous. Very small water samples (0.2 - 0.6 cc.) were taken from the remaining liquid for deuterium analysis.

Results

Figure 3 shows a plot of equation 14. Under conditions of reduced volumes of water and the assumptions given, it is

Figure 3. Plot of theoretical and experimental values of Q of equation 14 as a function of deuterium concentration for a water system of reducing volume


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Q (FRACTION EVAPORATED)
T = 25° C
EXPERIMENTAL
POINTS
EQUATION 14
1.0
1.1
1.2
1.3
1.4
1.5
x1 (EXPRESSED AS UNITS OF x0)

seen that the enrichment of deuterium is very large. The circular points in Figure 3 represent experimental values obtained by letting water evaporate in a closed system as described in the previous section. It is seen that the experimental points check well with the theoretical equation.

Figure 4 shows a plot of equation 19. Under constant volume conditions, we let $z = x_o$, and with the assumptions given, it is seen in Figure 4 that the maximum deuterium enrichment (x for $Q = \infty$) that could be expected was about 7 percent above the initial deuterium concentration. The enrichment becomes negligible after three times the initial volume of water has evaporated. At D concentrations found in normal water this increase is negligible, but it becomes more important at higher concentration.

Although equation 19 was not checked experimentally, its validity may be checked by equation 14, which was checked experimentally as shown in Figure 3. The relationship between these two equations will now be shown. By letting a finite amount of water evaporate from a hypothetical water system of volume V, the enrichment of the remaining water may be determined from Figure 3. The sloping parts of the saw-tooth curve in Figure 5 are actually short segments of the curve shown in Figure 3. The vertical rise in each of the saw-teeth corresponds to a change in Q of 0 - 0.2Q in Figure 3. The sloping parts of the saw-tooth curve then indicate DOH enrichments

Figure 4. Plot of theoretical values of Q of equation 19 as a function of deuterium concentration for a water system of constant volume

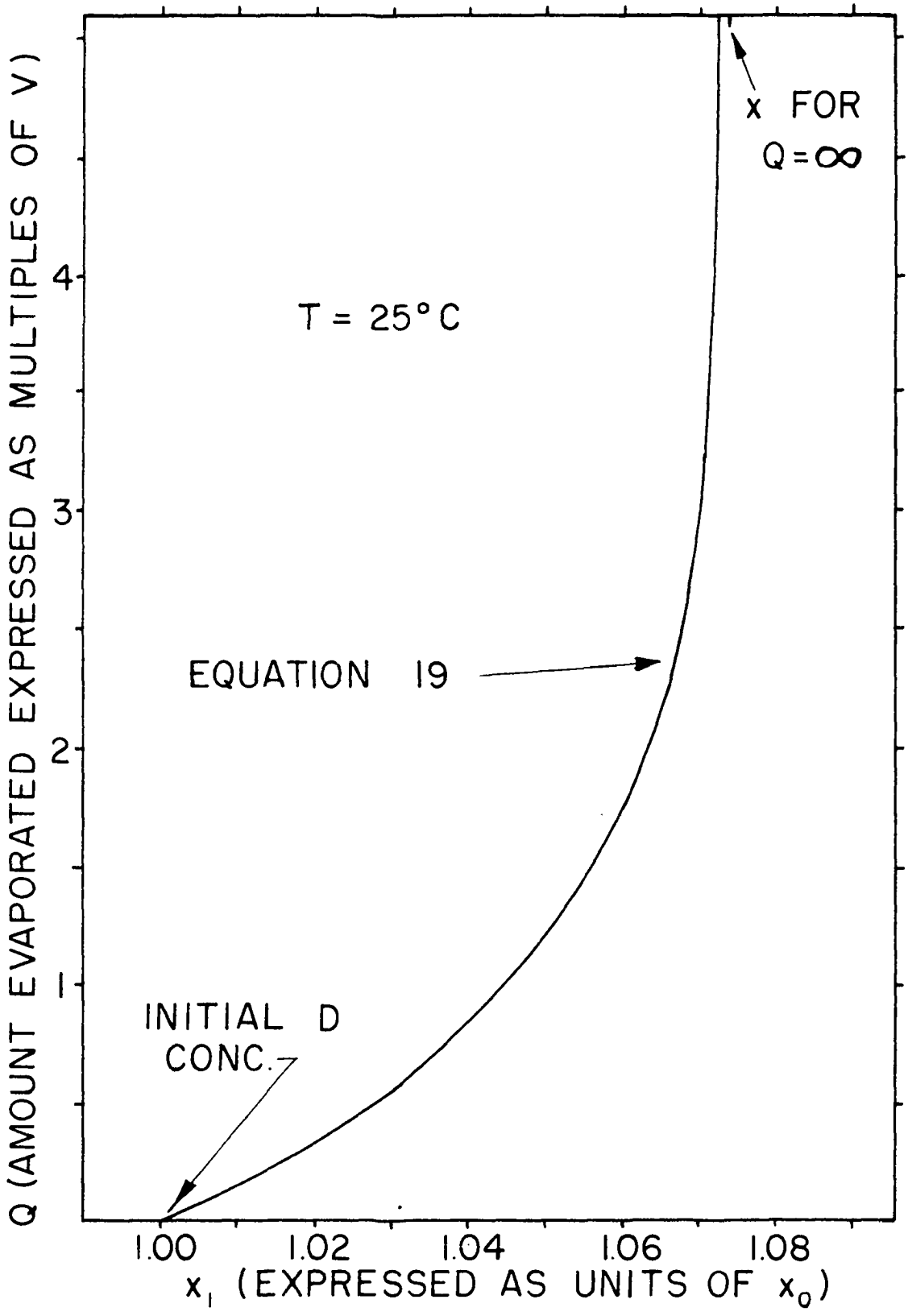
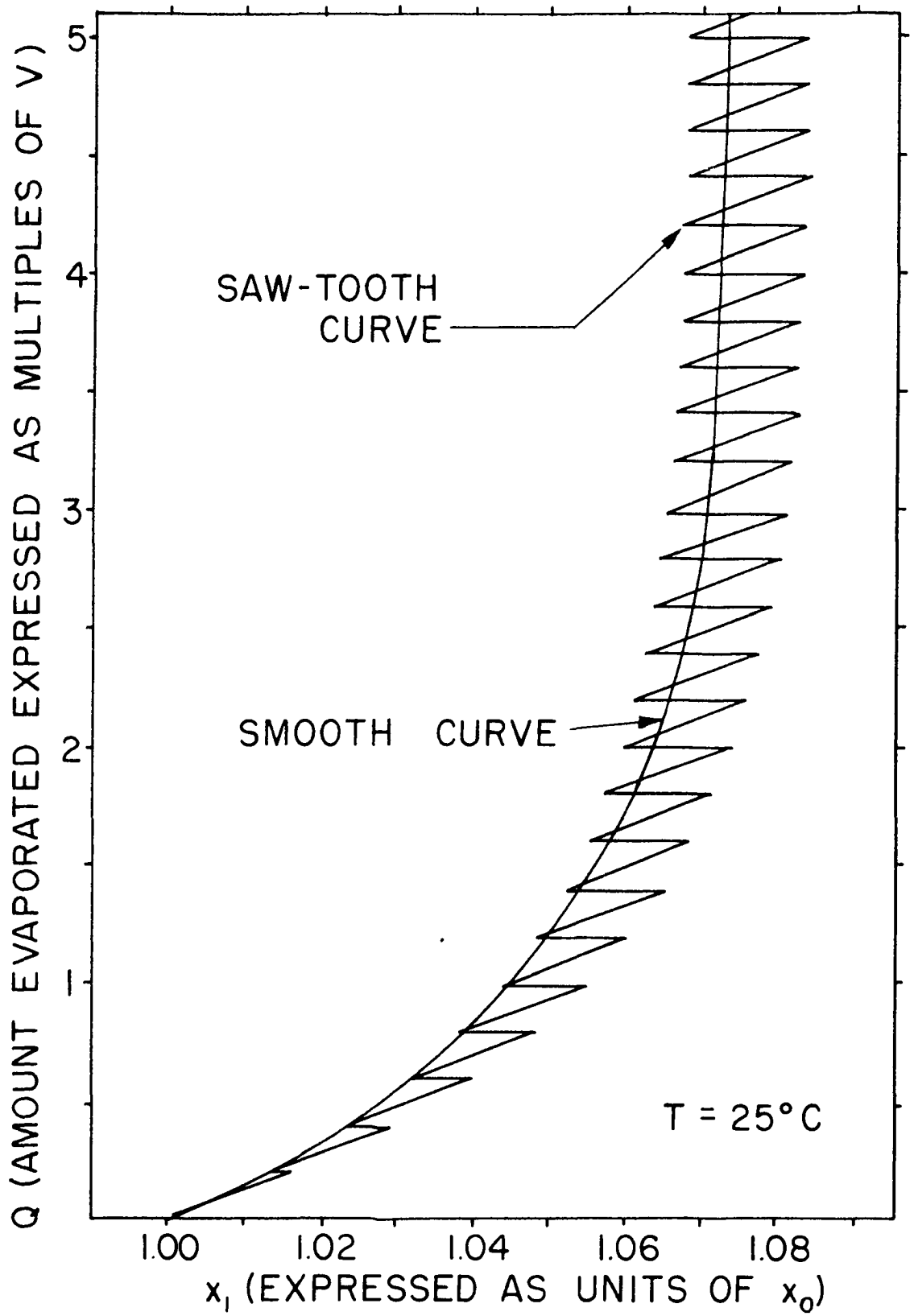

Q (AMOUNT EVAPORATED EXPRESSED AS MULTIPLES OF V)
4
3
2
1
x FOR
Q = ∞
T = 25° C
EQUATION 19
INITIAL D
CONC.
1.00
1.02
1.04
1.06
1.08
x1 (EXPRESSED AS UNITS OF x0)

Figure 5. Comparison of theoretical values of Q plotted as a function of the deuterium concentration when utilizing equation 14, saw-tooth curve, and equation 19, smooth curve


Q (AMOUNT EVAPORATED EXPRESSED AS MULTIPLES OF V)
5
4
3
2
1
SAW-TOOTH CURVE
SMOOTH CURVE
T = 25°C
1.00
1.02
1.04
1.06
1.08
x1 (EXPRESSED AS UNITS OF x0)

resulting from successive incremental additions of water. By making an incremental water addition of 20 percent of the initial volume to the system and with the D concentration of this addition equal to x_o, the deuterium concentration is reduced but not to its initial concentration. The 20 percent additions are made only after this amount has evaporated from the system. Thus the remaining volume plus the addition does not exceed the initial volume. The smooth curve in Figure 5 is the same plot as shown in Figure 4. It was inserted here so that a suitable comparison could be made between the two types of enrichment curves.

Discussion

From the test models it is quite conceivable that enrichment by distillation is taking place in plants. It is surprising, in view of the results of these calculations, that Washburn and Smith (49) found deuterium enrichments of only about 3 ppm. in willow tree sap. The low enrichment found by Washburn and Smith, as opposed to an enrichment of 10 ppm. found from the test model for water of similar D concentration, may be explained as a consequence of the assumptions of equations 14 and 19 not being met for the willow tree.

The D concentration of a Petri dish of water, when evaporating under atmospheric conditions, is influenced much more by the exchange of water vapor from the atmosphere than

by the enrichment process. A similar phenomenon must take place at the leaf surface of plants so that only a very slight enrichment could be expected with ordinary water. This was verified in an experiment in which oat plants were grown in 0.3 percent D culture solutions. Analyses were made of the leaf water periodically, but under no circumstances was an enrichment of DOH observed that was above or even approaching that of the culture solution. Thus, when one grows plants in culture solutions of higher D concentrations under normal atmospheric conditions, the untagged atmospheric water vapor will constantly dilute the tagged water in the leaves. The rate of this diluting process is affected externally by air temperature, wind velocity, and relative humidity. Physiologically, the size, the growth rate, and the transpiration rate of the plant itself also influence the dilution rate. These factors complicate the problem tremendously, and it is almost impossible to ascertain what the D concentration of a leaf should be under ordinary environmental conditions. On the basis of these results the findings of the work reported by Polyakow and Germogenova (37) in the "Literature Review" are questioned.

Thus the idea and the technique of utilizing the D concentration of leaf water as an index of water uptake from a particular soil region appear doomed to failure. Nevertheless the equations help clarify water movement processes that

occur in nature.

The harmony between the two equations which were independently derived and between the experimental data and equation 14 is an excellent indication of the validity of both enrichment equations. In Figure 5, the saw-tooth curve could be made to coincide exactly with the smooth curve if the evaporative losses and incremental additions of water were reduced to infinitisimal quantities.

In both of the derived mathematical equations the amount of water lost by evaporation is related to the enrichment of the remaining water. When attempting to evaluate the amount of water lost by evaporation it may be desirable to analyze the water vapor instead of the remaining liquid. The normal procedure is to plot y versus x as given in equation 11. From the measured values of y, values of x may be obtained. These are then substituted into equation 14 or 19. With very dilute solutions as were used in this experiment and with the vapor pressure ratio close to unity, y is very accurately approximated by

$$y = ax$$

This simplifies the derivation of equation 14 so that one obtains

$$\ln(1 - Q) = -\left(\frac{1}{a - 1}\right) \ln\left(\frac{y_o}{y}\right) \quad y_o < y$$

and similarly equation 19 reduces to

$$Q = -\frac{V}{a} \ln\left(\frac{z - y}{z - y_o}\right) \quad z > y_o, \quad y > y_o$$

With 1 percent concentrations of D the approximation produces an error in y which amounts only to 7 ppm. and with lower concentrations it is less. Seven ppm. is about the minimum error for D measurements with the mass spectrometer.

Uptake of Water by Plants

General

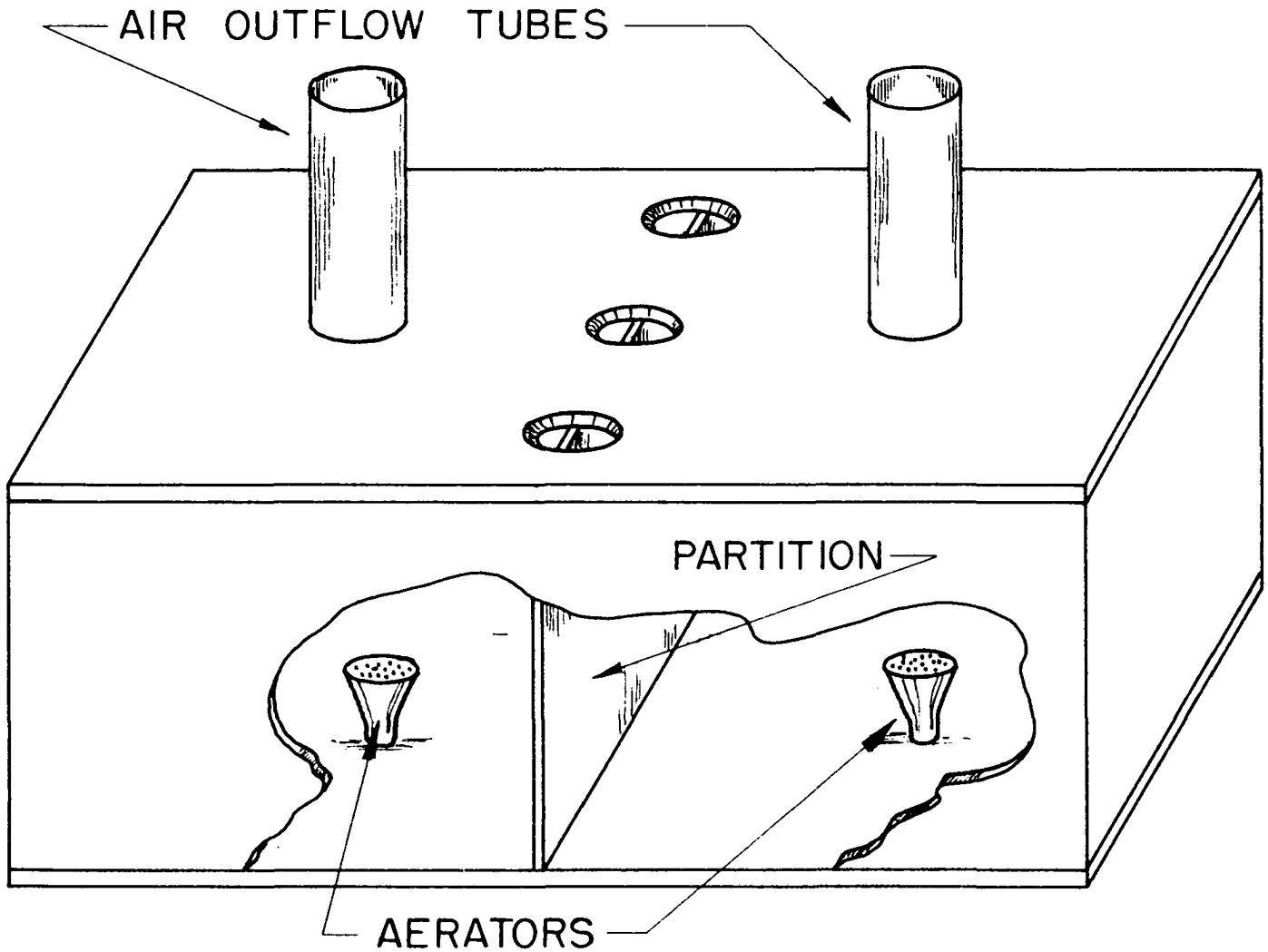
It has been seen that the uptake of water by plants can be studied by means of a split-root technique. Eaton (13), using this technique, calculated the water tension in plant xylem. We wish to use the technique to study the influence of different root environments upon water uptake. In the following the feasibility of such a procedure will be described on the basis of experiment. The first experiment reported does not involve the use of deuterium. Another experiment does involve deuterium. It will be mentioned.

Method

The nutrient or culture solution container, as shown in Figure 6, was constructed of 1/4-inch thick plexiglass with overall dimensions 9 inches long, 6 inches wide, and 6 inches deep. This container was partitioned into two equal volumes by cementing a thin piece (1/8-inch thick) of plexiglass to the 9 inch walls as shown in Figure 6.

To facilitate aeration of the culture solutions, small

Figure 6. Culture solution container used in growing plants under split root conditions


AIR OUTFLOW TUBES
PARTITION
AERATORS

fritted glass filters (aerators) were built into the bottom side of each half of the container. The inner wall surface of the top side above the aerators was machined to give a concave instead of a flat wall surface. This permitted the air bubbles from the aerators to collect there and these could then pass out of the container through the air outflow tube. A concave surface and a large outflow tube (3/8 inch, inside diameter) were necessary; otherwise air would force water out through the outflow tube. The container was covered with black plastic film to prevent penetration of light and attendant growth of algae.

Oat plants were germinated and grown to the seedling stage in a normal soil. When primary roots began to form, the seedlings were washed clean of soil and transplanted to the culture solutions. The roots of each of three seedling plants were inserted into separate holes of the top side of the container and then into both the separated chambers. The root system of each plant was distributed as evenly as possible between the two chambers. After a sufficient number of secondary roots were initiated by the plant, the space surrounding the crown and the area of attachment of the roots with the stem was sealed with a mixture of 5 parts paraffin, 2 parts beeswax, and 2 parts petrolatum.

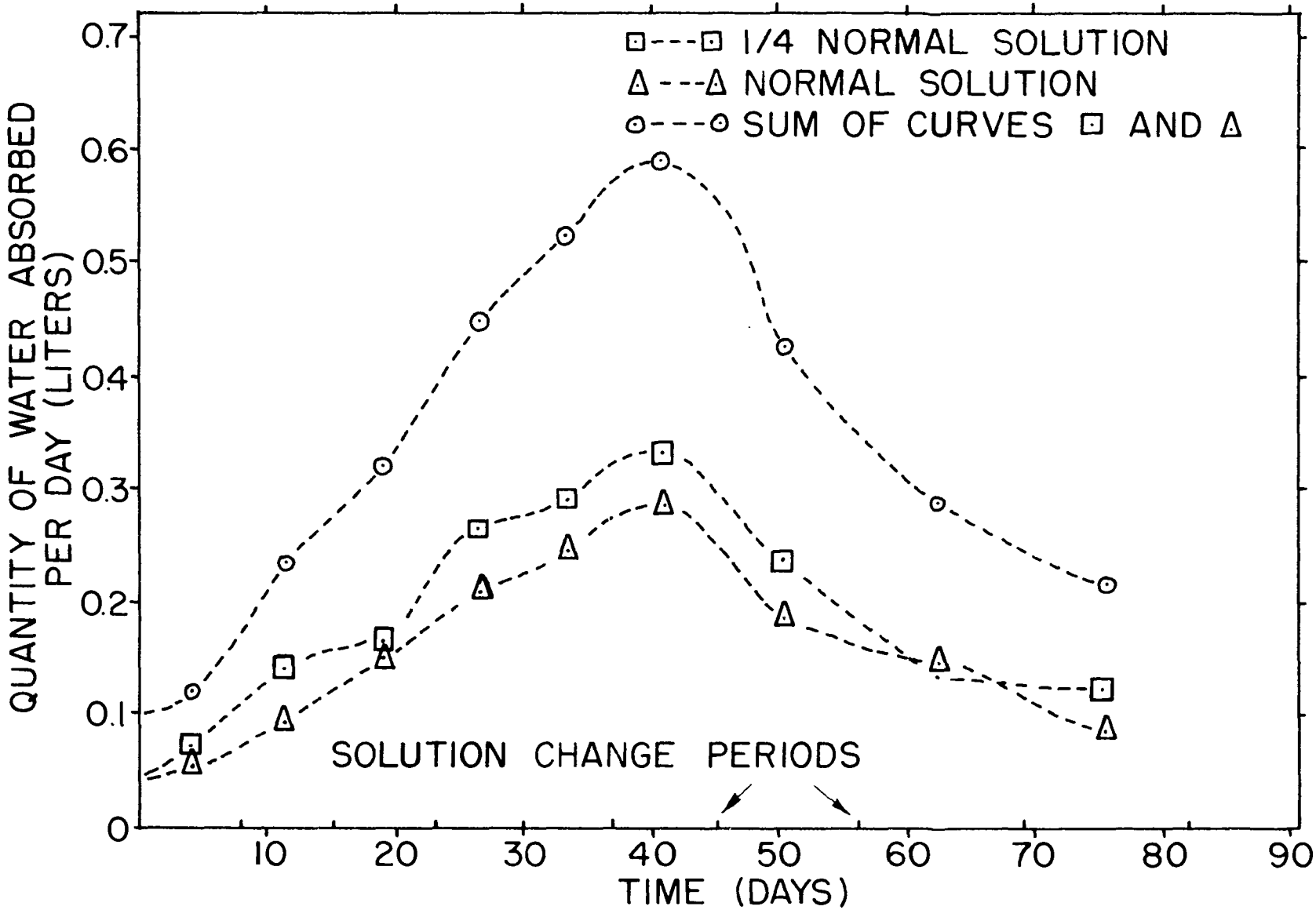
By placing nutrient solutions of two different concentrations in the two containers, plants were grown on the two

different nutrient concentrations simultaneously. The concentration of the solution was switched every 7 to 13 days between the two root systems. This was done to prevent growth differences which might result from a particular nutrient concentration level. Each day, needed water (resin-filtered tap water) was added to each root chamber. A daily account was kept of the water added and hence of the water uptake, as there was no evaporation. Electrical resistance measurements of the nutrient solution (an index of nutrient uptake) were taken before additional water was added. Fresh nutrient solution was always used when the concentration of solution was switched periodically from one chamber to the other. The concentrations of the nutrient solutions were always either 1 or 1/4 where "1" is defined as a normal Hoagland's nutrient solution (0.016 molar) as given by Hoagland and Arnon (17) and "1/4" is defined as a solution of 1/4th that concentration.

Results

The amounts of water absorbed by the two root systems are graphed in Figure 7. Each point represents the amount of water absorbed per day (as calculated for a time interval of 7 to 13 days), plotted as a function of the time that the plants have been in the culture solution. The successive points on the curve representing each culture solution stem

Figure 7. Quantity of water absorbed per day by plants in nutrient solutions plotted as a function of time


⊡---⊡ 1/4 NORMAL SOLUTION
Δ---Δ NORMAL SOLUTION
⊙---⊙ SUM OF CURVES ⊡ AND Δ
QUANTITY OF WATER ABSORBED PER DAY (LITERS)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
SOLUTION CHANGE PERIODS
10
20
30
40
50
60
70
80
90
TIME (DAYS)

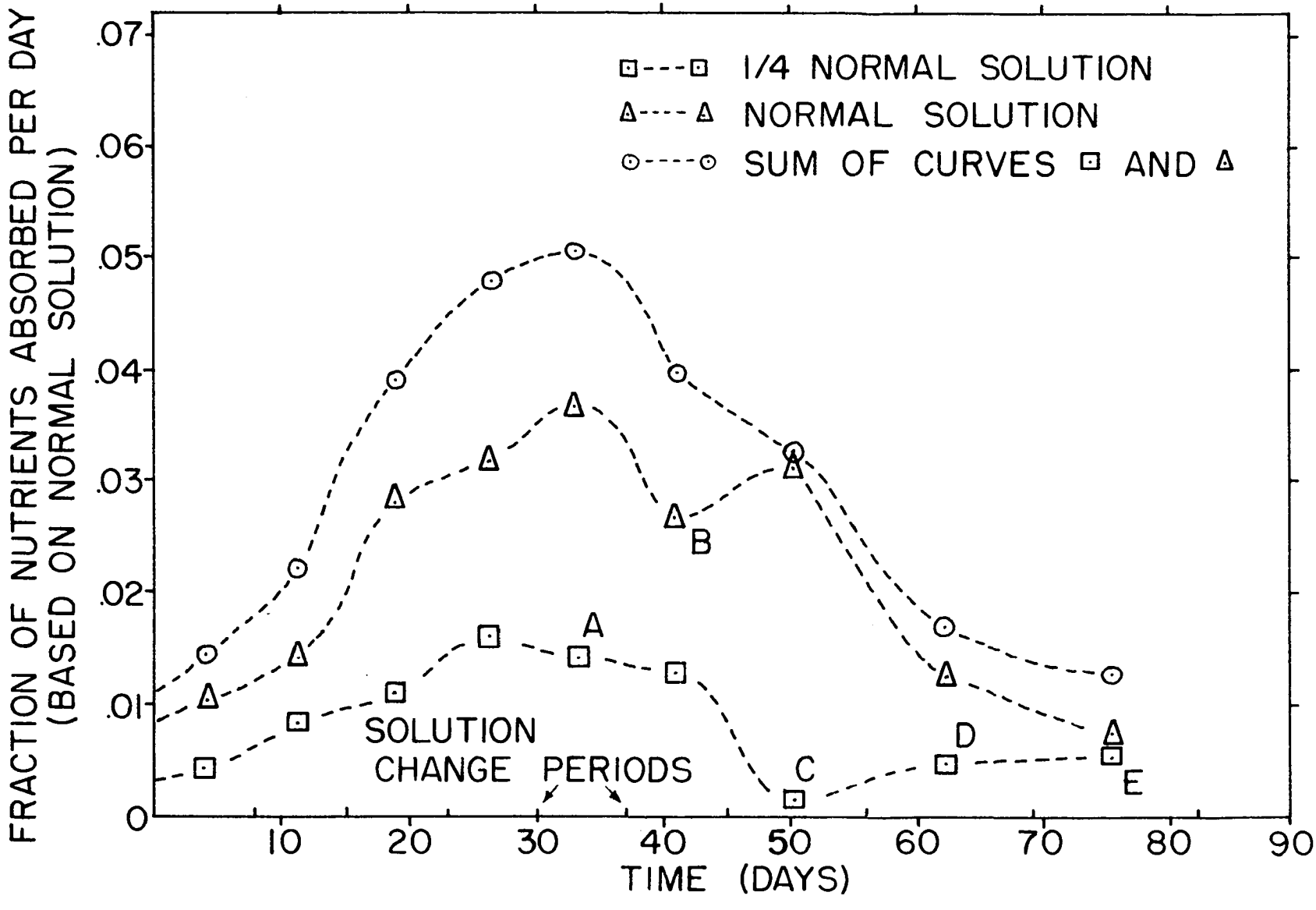
respectively from alternating root systems. Thus each root system in Figure 7 is represented by alternating squares and triangles.

The total amount of water absorbed was obtained from the sum of daily additions of water to each chamber. The total amount of water absorbed in 80 days from the chamber initially at unit concentration was 13.17 liters and from the 1/4 concentration, 15.06 liters. Therefore the percent difference in moisture uptake from the two concentrations was (15.06 - 13.17)/(15.06 + 13.17) x 100 = 6.7 percent.

In order to initiate flowering the "daylight period", controlled by artificial lighting, was changed from 12 to 14 hours 30 days after the experiment was initiated and seed heads were observed 22 days after the day length was changed. As may be observed from the graph, the 30 to 52 daytime period was the period of maximum water absorption for both root systems.

Figure 8, similar to Figure 7, shows the daily nutrient uptake by plant roots from each level of nutrient concentration and the sum of the absorbed nutrient uptake. Both nutrient uptake curves are plotted as a function of the time that the plants have been in the culture solutions. The nutrient uptake determinations were made from resistance measurements and are based on a system in which there is initially, in the case of normal Hoagland's nutrient solution,

Figure 8. Fraction of nutrients absorbed per day by plants in nutrient solutions plotted as a function of time, for points A, B, C, D, and E, see text


FRACTION OF NUTRIENTS ABSORBED PER DAY
(BASED ON NORMAL SOLUTION)
.07
.06
.05
.04
.03
.02
.01
0
10
20
30
40
50
60
70
80
90
TIME (DAYS)
1/4 NORMAL SOLUTION
NORMAL SOLUTION
SUM OF CURVES ⊡ AND Δ
SOLUTION
CHANGE PERIODS
A
B
C
D
E

a unit amount of nutrient. Since environmental conditions were the same in both root systems, except for the nutrient concentration and the resulting osmotic effects, it was assumed that if there was any preferential uptake of nutrients, it was solely due to a concentration-osmotic factor.

In Figure 8 certain points A, B, C, D, and E are singled out. These are for the same root system subjected to the alternate nutrient concentrations. Points B and C fall below their apparently normal positions on the curves denoted by triangles and squares. This root system thus appears to be absorbing nutrients at a lower rate; however, this rate returns to normal between 60 and 70 days since points D and E seem to fall on their normal curve again whereby normal curves are meant curves in which the dips would not have occurred.

Discussion

The total water absorbed for the 1/4 normal solution was 6.7 percent greater than for the normal solution. This difference may be explained by osmosis. After a period of about 60 days after initiation of the experiment there appeared to be (Figure 7) a preferential uptake of water from one of the root systems as is observed from the cross-over of the curves. This preferential uptake could be explained on the basis of a slightly greater amount of root surface for the root system in question.

Although no deuterium measurements were taken in this study, there was carried out a separate deuterium experiment, not to be mentioned further, showing that under similar experimental conditions there was no water flow through the roots from one root system to the other, at least not to the extent that it was detectable.

In Figure 8 the differences for the uptake of nutrients from the two individual solutions were greater than for the case of the uptake of water. It may be observed that throughout the experiment there was greater absorption from the stronger solution. However, relative to the concentration, there was greater absorption, with one exception (point C in Figure 8), from the weaker solution because the uptake of 1/4 normal solution multiplied by 4 exceeds the uptake of the normal solution. Therefore the exception that occurred for point C at the 50-day period is not readily explainable. The displacement of point C is believed not to be due to error, but rather due to an unexplained physiological condition associated with this half of the root system or with the entire plant. The anomalous nutrient uptake occurred during the period of flowering. During the anomalous time (about 10 days) it appeared that no nutrients were being absorbed from the weaker solution. From the daily solution concentration measurements taken it even appeared that for a short period of time ions were moving from the strong solution

through the root system into the weaker solution because the weaker solution became slightly more concentrated.

It may be observed by comparing Figures 7 and 8 that the curve patterns for the combined water uptake and combined nutrient uptake are somewhat similar throughout the experiment. However, the uptake of nutrients and water for individual systems is quite different, especially at the time of seed head appearance. Although there appeared to be preferential uptake of nutrients by one root system, this did not occur for water uptake except at the time when the curves crossed over in Figure 7. However, preferential water uptake was observed to occur in the opposite root system in which preferential absorption of nutrients occurred.

This experiment points out that nutrient concentration will have to be very similar when studying water uptake by plants under split-root conditions. Since the anomalous nutrient uptake occurred at the time of flowering one may conclude that the flowering period would be a difficult one to work with in split-root studies. But if one is to work with this period controls can be affected by determining the rate of water absorption from both root systems immediately before imposing a diverse environment.

Proposed Future Work for Plant Experiments

Although the technique of utilizing the D concentration of leaf water as an index of water uptake from a particular soil region has been seen, in the "Discussion" following Figure 5, not to be satisfactory, nevertheless a procedure which is now given appears to be a satisfactory approach to the problem. The procedure calls for a split-root technique and tagged soil water. In addition, the procedure calls for a small plant canopy to be used so that atmospheric water vapor will not contaminate the water transpired by the plants. Air, dried in a CO_2-alcohol moisture trap, would be circulated through the canopy at a rate that would keep the relative humidity low. The partially moisture-laden air in the canopy would then be passed through another CO_2-alcohol moisture trap to remove the transpired water. Whenever a differential root environment is to be imposed on the two root systems, moisture samples would be collected every 5 to 10 minutes and examined for deuterium content. From the total amount of water and the proportion of tagged water collected the effect of the less favorable root environment could then be determined. By returning the plant roots to a normal environment, the duration of the after-effects from the adverse environment also could be studied. Some possible adverse environments that could be studied are high and low temperatures, low oxygen concentrations, and high CO_2 concentrations.

Conclusions of Plant Experiments

1. It was shown that under certain laboratory conditions enrichment of DOH in DOH-HOH mixtures did result. Enrichment of plant leaf sap under ordinary environmental conditions cannot be detected because of exchange occurring between leaf sap and atmospheric water vapor.

2. Two enrichment equations were derived for ideal water systems, one for a water system of decreasing volume and one for a water system of constant volume. In both cases the degree of enrichment could be calculated by the quantity of water evaporated.

3. An example was shown where one equation was utilized in place of the other in calculating the enrichment effect. The close harmony between experimental data and one of the theoretical curves and between the two theoretical curves when adapted to similar experimental conditions indicates the validity of the two equations.

4. The tests with the above equations show that deuterium enrichment may be used advantageously in studying rates of evaporation and possibly evapotranspiration under specific laboratory conditions.

5. Plants grown simultaneously in two nutrient solutions of different concentration for a period of 80 days showed that plant water uptake was 7 percent greater from the weaker solution than from the more concentrated solution.

6. Total nutrient uptake was greater from the more concentrated solution; however, when considering uptake on the basis of nutrient concentration, it was less.

7. The technique of split-root experiment described (without deuterium) should be of value in obtaining a better understanding of some plant-water relationships. A split-root technique used in conjunction with deuterium as a tracer can supply additional unknown information of plant response to different root environments.

SOIL EXPERIMENTS

Purpose of Experiments

A large amount of work has been conducted in the field of soil moisture movement. Although tracers (tritium, electrolytes) have been used in ground water studies, that is saturated flow problems, very little is known how effective they may be in determining water movement in the unsaturated state. Because soil water movement occurs in both the liquid and vapor phases, the use of hydrogen isotopes as water tracers is more efficient in detecting water movement than ions such as chlorides.

The objectives of the soil experiments were three-fold, and they are as follows: 1) develop a simple technique of quantitatively extracting tagged moisture from soil and analyzing the moisture for its D content; 2) determine under what circumstances a hydrogen tracer could be used advantageously, as opposed to other tracers and methods, in studying unsaturated soil water movement; and 3) concentrate on the phases of the second objective that appear to justify further research.

To accomplish the objectives, experiments were done on the mass flow of water and the diffusion flow of water. Ungapped and gapped soil cores were used for the mass flow experiments. The gaps would prevent continuous film flow

since the flow across the gaps would have to be by vapor. Ungapped cores were used for the diffusion flow studies. The only type of diffusion studied was self-diffusion.

Mass Flow of Soil Water in Gapped and Ungapped Cores

Introduction

Soil water evaporation is a major problem in agriculture. Accurate information is not known at what depths evaporation or (distillation) occurs in the soil. Therefore an experiment utilizing heavy water as a tracer was conducted to see where the evaporated water originated in the soil profile and how much evaporated water was carried upward by water flow in various stages of the unsaturated state. By applying tagged water to a section of the soil profile, its movement could be followed by periodically taking a small soil sample and analyzing the water.

Method

The experimental procedure consisted of packing soil that was uniformly moist into three plexiglass cylinders, 3 inches in diameter and 2 inches in height. These cylinders were fastened together, end to end, with scotch electrical tape so that a 6-inch long soil core resulted. The 6-inch core would correspond to plow layer depth in arable land. Untagged

water was used to moisten the soil in both upper and lower cylinders and tagged water was used to moisten the soil in the middle cylinder. The fused soil core was placed in an upright position. The lower end of the soil core was sealed. A small air-tight canopy was fastened to the upper end of the core. Dry air could be and was then passed over the soil surface to pick up moisture. Because the soil moisture in the cores was about at field capacity, any movement due to gravity in these upright cores would be small and it would be in the opposite direction of the movement induced by the dry air passed over the soil surface.

After the dry air was circulated in the canopy and the air had become moist, it was forced through a moisture cold-trap where the water vapor was removed. The cold-trap was kept cold by a solid CO_2-alcohol mixture. Since it is colder and therefore more efficient in condensing water, a liquid-nitrogen trap would appear to be preferred to a solid CO_2-alcohol trap; the latter was used so that oxygen in the moist air would not liquefy. Water samples were collected periodically from the moisture trap and were analyzed for D content. Small soil samples were removed from the soil core at 70 hours from the beginning of the experiment and these samples were tested for D content and moisture content. After 140 hours the evaporating portion of the experiment was concluded.

A second experiment, conducted over a period of 170 hours,

was done in a similar manner except that the soil core was prepared to have two gaps, each separating the tagged and untagged soil. These gaps were at the one-third and two-thirds length of the composite core.

After arbitrary periods of 140 and 170 hours, respectively, the ungapped and gapped soil cores were sliced up into nine sections of equal length (about 1.7 cm.). The sections were analyzed for moisture content and D content. To recover the water from the sectioned soil core segments and from soil samples removed from the cores at 70 hours, the soil samples were placed in glass tubes and were vacuum-dried. The water vapor was condensed in a liquid-nitrogen cold-trap. To speed up the removal of liquid water from the soil sample, the glass tubes containing the soil samples were placed in an annular heating-oven maintained at 105° C. The drying period used was 1 to 2 hours. The average size of soil sample from which the sample water was extracted was 5-10 grams. The glass tubes in which the samples were dried were 2.5 cm. in diameter and 25 cm. in length. Under rapid vaporization it was necessary to filter soil particles out of the water vapor stream. This was accomplished by placing a small plug of glass wool in the tube over the soil sample. After the drying period was completed, the frozen water samples were melted and removed from the trap. The samples were then broken down into hydrogen isotope gases and calcium hydroxide, employing the same

technique as was used for the breakdown of the water standards. The analysis of the samples with the mass spectrometer was identical with that previously described.

Results

The quantity of tagged-plus-untagged soil water in the ungapped and gapped cores are shown respectively at the left and right of the upper half of Table 1. The values are the amounts of water found in each cylindrical section of the cores at the indicated depth and time. The final time, 140 and 170 hours, is not the same for the gapped and ungapped cores. The values in lower half of Table 1 are corresponding values for tagged water. The lower line of the upper half and of the lower half of the table gives the amount of each type of water evaporated for the two cores. In all cases the total amount removed by evaporation was obtained by difference between initial and later moisture contents. Moisture percentages by volume for the moisture values given in Table 1 may be obtained, but are not recorded in Table 1, by dividing the volume of water in cc. by 228 cc., the volume of each cylindrical section.

In Figure 9 the volume percentage of the tagged moisture in the ungapped core at t = 0 and t = 140 hours is plotted versus the distance from the evaporating surface. The same type of data is given in Figure 10 for the gapped core for

Table 1. Quantity of tagged-plus-untagged water and quantity of tagged water in ungapped and gapped soil cores; also amount of these waters evaporated from ungapped and gapped soil cores for various time periods

	Ungapped core Time (hrs.)			Gapped core Time (hrs.)		
	0	70	140	0	70	170
Depth (inches)	cc. of tagged-plus-untagged water			cc. of tagged-plus-untagged water		
0 - 2	97.6	67.1	44.7	91.7	50.8	33.2
2 - 4	95.8	77.6	67.9	83.0	76.5	74.6
4 - 6	95.7	77.3	69.5	91.0	86.9	83.6
Total	289.1	222.0	182.1	265.7	214.2	191.4
Amount evaporated (cc.)	0.0	67.1	107.0	0.0	51.5	74.3
Depth (inches)	cc. of tagged water			cc. of tagged water		
0 - 2	0.0	20.9	24.6	0.0	8.0	14.5
2 - 4	95.8	59.1	40.4	83.0	57.0	42.2
4 - 6	0.0	8.4	13.2	0.0	12.6	18.7
Total	95.8	88.4	78.2	83.0	77.6	75.4
Amount evaporated (cc.)	0.0	1.6	9.1	0.0	0.3	3.0

Figure 9. Tagged moisture percent at t = 0 and t = 140 hours in an ungapped soil core

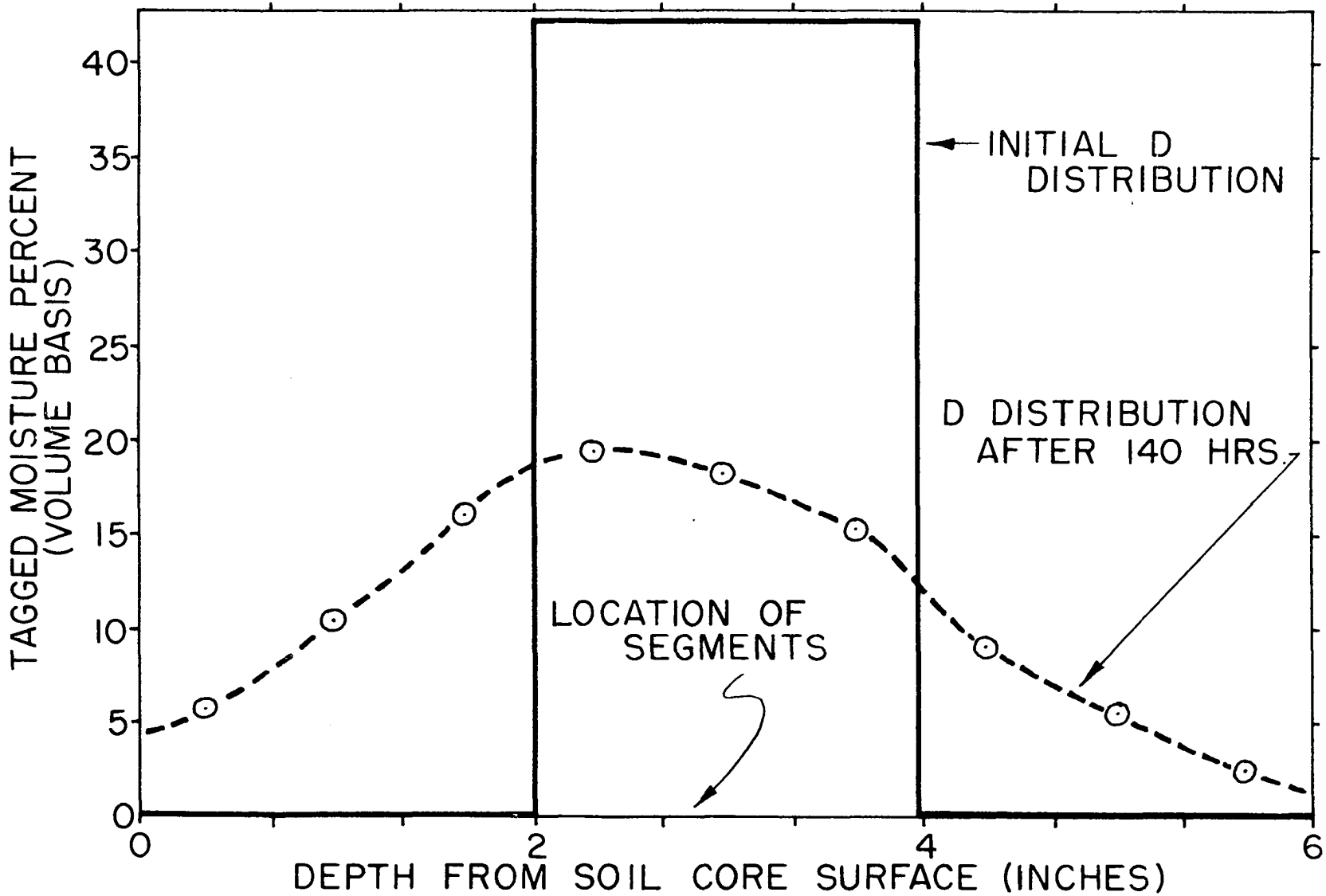
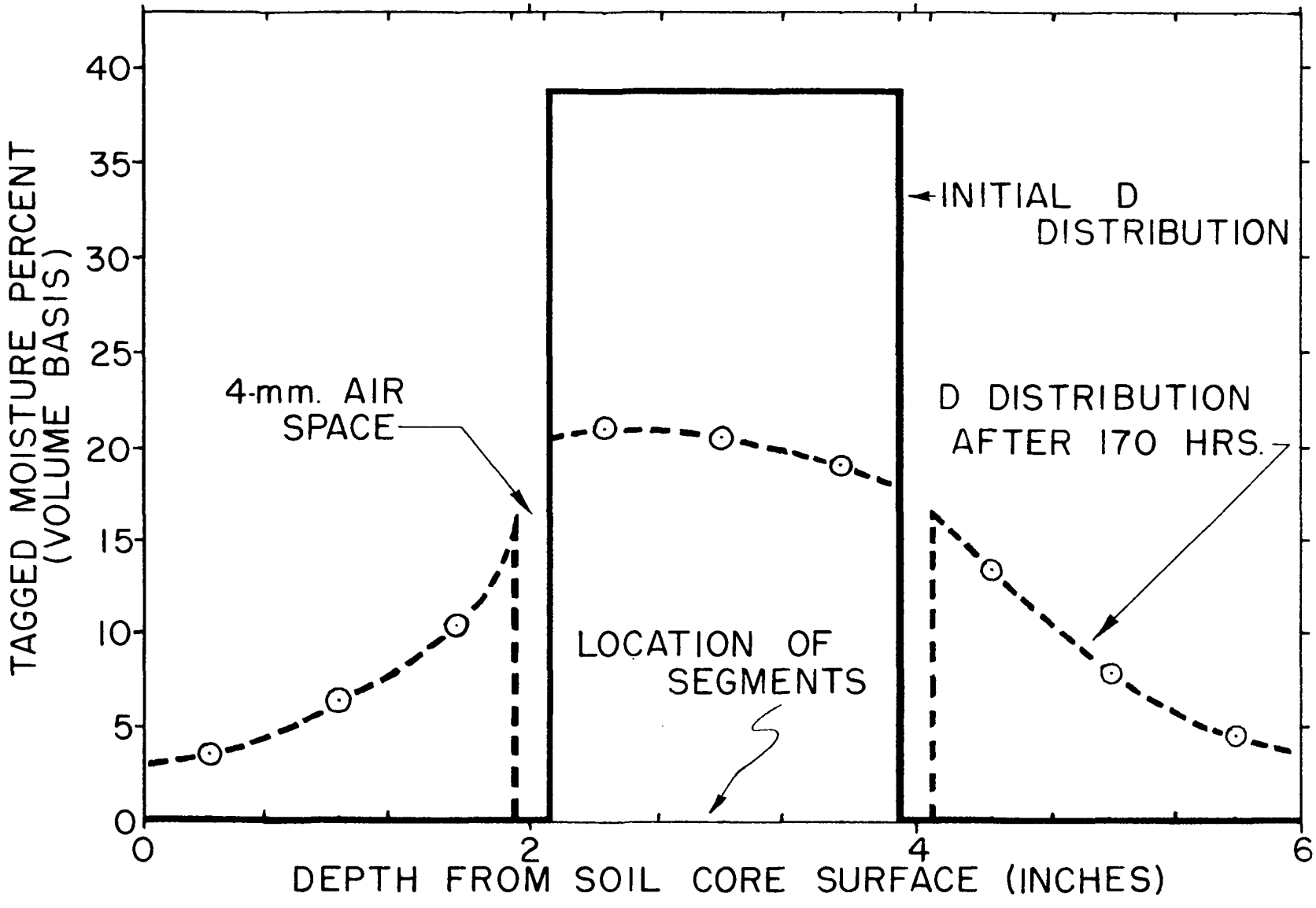

TAGGED MOISTURE PERCENT (VOLUME BASIS)
40
35
30
25
20
15
10
5
0
0
2
4
6
DEPTH FROM SOIL CORE SURFACE (INCHES)
INITIAL D DISTRIBUTION
D DISTRIBUTION AFTER 140 HRS.
LOCATION OF SEGMENTS

Figure 10. Tagged moisture percent at t = 0 and t = 170 hours in a gapped soil core


TAGGED MOISTURE PERCENT (VOLUME BASIS)
40
35
30
25
20
15
10
5
0
0
2
4
6
DEPTH FROM SOIL CORE SURFACE (INCHES)
INITIAL D DISTRIBUTION
4-mm. AIR SPACE
D DISTRIBUTION AFTER 170 HRS.
LOCATION OF SEGMENTS

which t = 170 hours.

Discussion

By comparing the moisture values for both cores in Table 1 it is seen that gapping the core reduced the amount of total water evaporated from the lower two sections by about 68 percent. This value would have been larger had the time periods been equal. The quantity of water lost from the lower two sections of the gapped core had to move through the gap in the vapor phase. Other factors being equal, the difference in the amount of water lost from the lower two sections of the two cores may be attributed to mass water flow or diffusion in the liquid phase.

If one compares the overall shape of the curves in Figures 9 and 10, it is seen that the shapes are about the same. Thus, the mixing of the tagged and untagged water was not significantly hindered by gapping the core, even though the net amount of water passing through the gapped core was considerably less than that passing through the ungapped core.

Although self-diffusion of water is very evident in the gapped core, the net amount of water moved in the direction of the moisture gradient by vapor diffusion in the gapped core is very small. This fact may be observed (Table 1) by the small changes of total moisture content for the lower two sections of the gapped core. The constancy in water content

for these sections apparently is due to the small differences in the relative humidity of the soil air. Nearer to the soil surface the change in the relative humidity may be of the order of 70-80 percent over a very short distance. Under these larger gradients the net effect of vapor diffusion apparently plays a vital role in water movement.

The large amount of self-diffusion that occurred in these two experiments indicates a limitation in the use of heavy water and the technique as described above for measuring moisture flow in the unsaturated state. Apparently before any measurements of net water movement can be made by the technique described here, the magnitude of the self-diffusion process will have to be determined. To measure the self-diffusion coefficient an experimental technique is desired which will yield results lending themselves to mathematical analysis. A rigorous mathematical analysis of the self-diffusion phenomenon was not practical in the two evaporation experiments above because of non-steady state conditions. In a later section mathematical equations are derived that are useful in determining the magnitude of the self-diffusion coefficient.

We return, with a final comment, to Table 1. It may be observed in Table 1 that the amount of tagged water generally decreased as time progressed. Undoubtedly this loss of the tagged water molecules is the result of exchange occurring

between water and the clay minerals. Before self-diffusion coefficients can be determined with any degree of accuracy, this 6-9 percent loss of D will have to be corrected for or somehow circumvented. This matter will be taken up in the next section.

D Exchange between Water and Clay-Minerals

Method for testing exchange

Faucher and Thomas (14), Romo (39), and other investigators have shown that some exchange occurs between tagged water and the untagged hydroxyl groups of the clay lattice. In the soil water evaporation experiment discussed previously this type of exchange must also have taken place because the quantity of tagged water accounted for was less at the end of the experiment than at its beginning. To see if this loss could be avoided by use of a different experimental technique, a new experiment was undertaken. In this new experiment 10 gram quantities of Colo clay loam soil with moisture contents at 27.46, 23.30, and 17.40 percent by weight, and of known D content, were mixed with 10 gram quantities of the same soil materials with moisture contents at 27.10, 23.41, 18.36, and 12.52 percent by weight. The moisture of the latter samples was natural water and hence the D content in the latter samples was that of normal water. Twelve composite samples were placed in test tubes and allowed to equilibrate

for a period of 1 week. At that time the total moisture was extracted from each composite sample and an analysis made of its D content. By knowing the initial and final D concentrations and the moisture content of the soil materials it was possible to determine the quantity of D which was unaccounted for in the extracted water and which must have remained in the crystal lattice.

Results

The data, showing the amount of D which was accounted for as being lost, at the conclusion of this experiment are given in the last column of Table 2. Other pertinent data, not to be mentioned further, regarding this experiment are also given in Table 2. The last column of Table 2 shows that the average loss for the 12 experiments was 2.09 percent of the calculated value for the composite sample. With some materials a larger, instead of a smaller, D concentration may be found at the end of an equilibration period. With materials such as glass beads (with which some experiments are to be reported subsequently), the chances of getting a larger value are just as probable as getting a smaller one because there will be negligible exchange and errors will be random ones.

Table 2. D concentration unaccounted for when mixing soil materials of known moisture and D content with soil materials of different moisture and D content and allowing the mixtures to equilibrate one week at room temperature

Sample number	Moisture %[c] of tagged soil	Moisture % of untagged soil	D conc.[a] of water in tagged soil	Calculated[b] D conc. of composite samples	Measured D conc. of composite samples	D conc. lost (ppm.)	%[d] D lost
1	27.46	27.10	2269	1210	1193	17	1.41
2	27.46	23.41	2269	1282	1260	22	1.72
3	27.46	18.36	2269	1388	1335	53	3.82
4	27.46	12.52	2269	1550	1513	37	2.39
5	23.30	27.10	2126	1070	1047	23	2.15
6	23.30	23.41	2126	1138	1133	5	.44
7	23.30	18.36	2136	1238	1196	42	3.51
8	23.30	12.52	2126	1393	1382	11	.79
9	17.40	27.10	2064	927	910	17	1.83
10	17.40	23.41	2064	991	983	8	.81
11	17.40	18.36	2064	1088	1061	19	1.90
12	17.40	12.52	2064	1243	1189	54	4.34

[a]Conc. is given in ppm., that is parts of D per million parts of (D + H).

[b]$\text{Calculated D conc.} = \dfrac{(H_2O\% \text{ of tagged soil})(\text{D conc.}) + (H_2O\% \text{ of untagged soil})(\text{D conc.})}{H_2O\% \text{ of composite soil sample}}$.

[c]Moisture % is given on an oven-dry basis.

[d]% D lost = (D conc. lost)/(calculated D conc. of composite samples) x 100.

Discussion

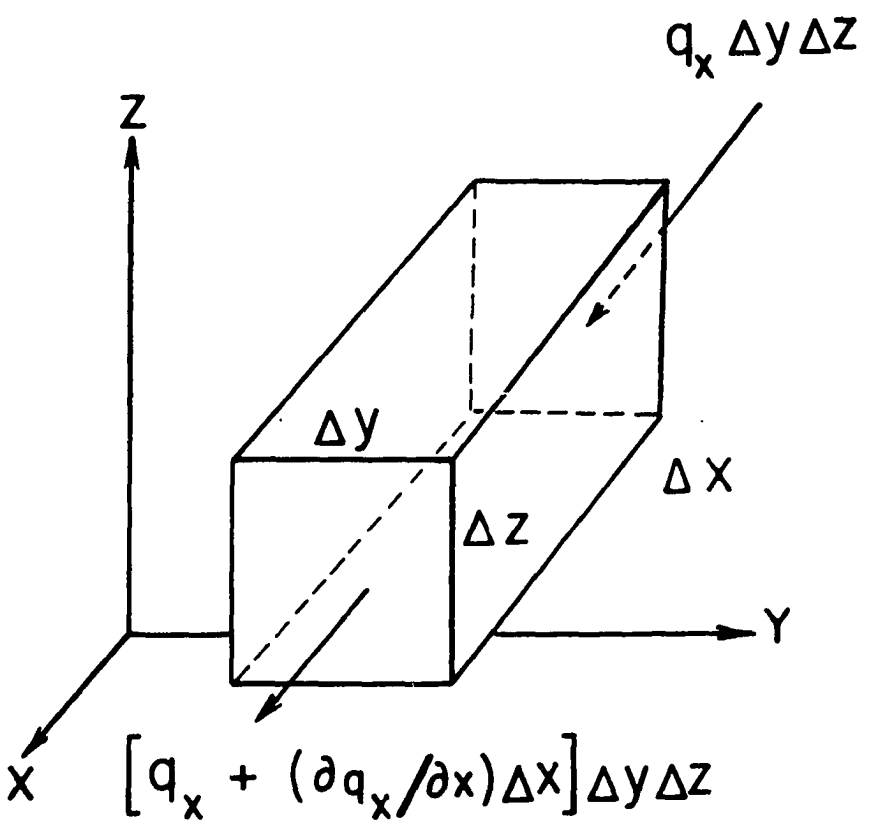
The very small losses of D that were observed in this experiment indicate that exchange processes will not be a major hindrance in measuring the self-diffusion coefficient of soil moisture. It has been observed in exploratory work, not reported herein, that losses, much greater than observed here, occur when adding tagged water to a dry and previously untagged soil. This large loss does not occur in the self-diffusion experiments of soil water where half of the soil used in the experiment is equilibrated with tagged water. The small losses that are observed are probably due to electrostatic or other atomic forces associated with the heavier isotope. Any loss of D in an exchange process with the previously untagged portion of soil is corrected by a gain of D from the tagged portion. What effect this dynamic exchange has on the magnitude of the self-diffusion coefficient has not been established, but rough calculations, not presented here, indicate this effect is not important.

Self-Diffusion Measurements of Soil Water

Derivation of the self-diffusion equation

Consider the x-component of flow in a parallelepiped of edges x, y, and z as shown in Figure 11. Let q_x be the number of deuterium atoms in a unit volume of water crossing a unit

Figure 11. Rectangular parallelepiped showing inflow and outflow of tagged water molecules in the x-direction


$q_x \Delta y \Delta z$
Z
Δy
Δx
Δz
Y
X
$[q_x + (\partial q_x/\partial x)\Delta x]\Delta y \Delta z$

area perpendicular to the x-direction. Then entering the back face are $q_x \Delta y \Delta z$ deuterium molecules per unit time and leaving the front face are $\left[q_x + (\partial q_x/\partial x)\Delta x\right]\Delta y \Delta z$ deuterium molecules. The number of deuterium molecules accumulated in the parallelpiped per unit time is

$$q_x \Delta y \Delta z - \left[q_x + (\partial q_x/\partial x)\Delta x\right]\Delta y \Delta z = -(\partial q_x/\partial x)\Delta x \Delta y \Delta z$$

Similarly the number of deuterium molecules accumulated in the parallelepiped due to the y-component of flow is

$$-(\partial q_y/\partial y)\Delta x \Delta y \Delta z$$

and due to the z-component of flow

$$-(\partial q_z/\partial z)\Delta x \Delta y \Delta z$$

so that n, the net number of molecules accumulated per unit time in the parallelepiped, is

$$(\partial/\partial t)(n \Delta x \Delta y \Delta z) = -\left[(\partial q_x/\partial x) + (\partial q_y/\partial y) + (\partial q_z/\partial z)\right]\Delta x \Delta y \Delta z \qquad (20)$$

Now the number n of deuterium molecules per unit volume of water is also

$$n = A_o \rho \left[N_D/(N_D + N_H)\right]/M \qquad (21)$$

N is the number of molecules per cc. when A_o is Avogadro's number (6.02×10^{23} molecules per gram mole); M is the molar weight of the water in grams per gram mole (of value between 18.02 and 20.03 grams per mole depending on the concentration of the deuteriated water under consideration); and ρ is its density in grams/cc. Equation 21 may be written in briefer

form by the use of equation 1. The result is

$$n = A_o \rho C/M \tag{22}$$

so that the number of deuteriated water molecules in the parallelepiped is

$$n \Delta x \Delta y \Delta z = (A_o \rho C/M) \Delta x \Delta y \Delta z$$

and the increase per unit time of the number of molecules in the parallelepiped is

$$(\partial n/\partial t) \Delta x \Delta y \Delta z = \left[(A_o \rho/M)(\partial C/\partial t)\right] \Delta x \Delta y \Delta z \tag{23}$$

Combining equations 20 and 23, one obtains

$$(A_o \rho/M)(\partial C/\partial t) = -\left[(\partial q_x/\partial x) + (\partial q_y/\partial y) + (\partial q_z/\partial z)\right] \tag{24}$$

But the diffusion law as given in Crank (10, p. 2) is

$$q_x = -D_x(\partial n/\partial x) \tag{25a}$$

$$q_y = -D_y(\partial n/\partial y) \tag{25b}$$

$$q_z = -D_z(\partial n/\partial z) \tag{25c}$$

Substituting equations 25a, 25b, and 25c into equation 24, one obtains

$$\begin{aligned}(A_o \rho/M)(\partial C/\partial t) = -\{&\left[\partial/\partial x\right]\left[-D_x(\partial n/\partial x)\right] \\ &+ \left[\partial/\partial y\right]\left[-D_y(\partial n/\partial y)\right] \\ &+ \left[\partial/\partial z\right]\left[-D_z(\partial n/\partial z)\right]\}\end{aligned} \tag{26}$$

Now by substituting equation 22 into the right side of equation 26 and assuming D_x is independent of x, D_y is independent of y, and D_z independent of z, it follows that

$$(A_o \rho / M)(\partial C/\partial t) = D_x\left[(\partial^2/\partial^2 x)(A_o \rho C/M)\right] + D_y\left[(\partial^2/\partial^2 y)(A_o \rho C/M)\right] + D_z\left[(\partial^2/\partial^2 z)(A_o \rho C/M)\right] \quad (27)$$

By simplification of equation 27, the basic diffusion equation is

$$\partial C/\partial t = D_x(\partial^2 C/\partial x^2) + D_y(\partial^2 C/\partial y^2) + D_z(\partial^2 C/\partial z^2) \quad (28)$$

If it is further assumed that for an isotropic material the diffusion coefficients are the same, then equation 28 reduces to

$$\partial C/\partial t = D(\partial^2 C/\partial x^2 + \partial^2 C/\partial y^2 + \partial^2 C/\partial z^2) \quad (29)$$

In this problem self-diffusion is considered in the x-direction only and equation 29 reduces to

$$\partial C/\partial t = D_s(\partial^2 C/\partial x^2) \quad (30)$$

where D has now been changed to D_s so that the self-diffusion coefficient will not be confused with that of the moisture gradient diffusion coefficient, D, commonly used elsewhere.

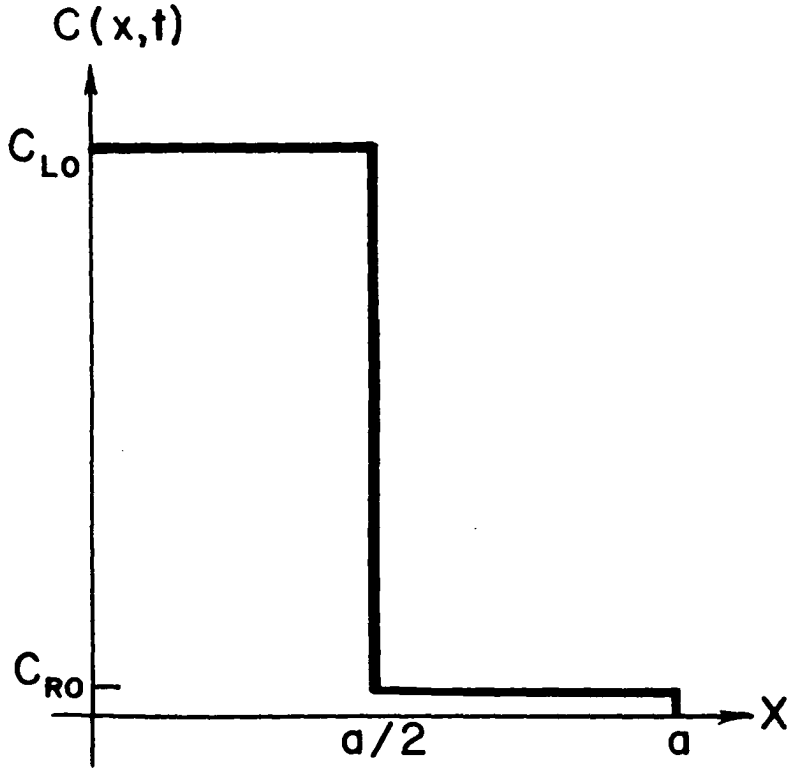
A drawing of the initial condition of the experimental system is shown in Figure 12. Let C_{LO} be the average concentration of D on the left half of the soil core at t = 0, and let C_{RO} be the corresponding quantity for the right half. Then the initial conditions for equation 30 are

$$C = C_{LO} \text{ for } t = 0 \text{ at } 0 < x < a/2 \quad (31)$$

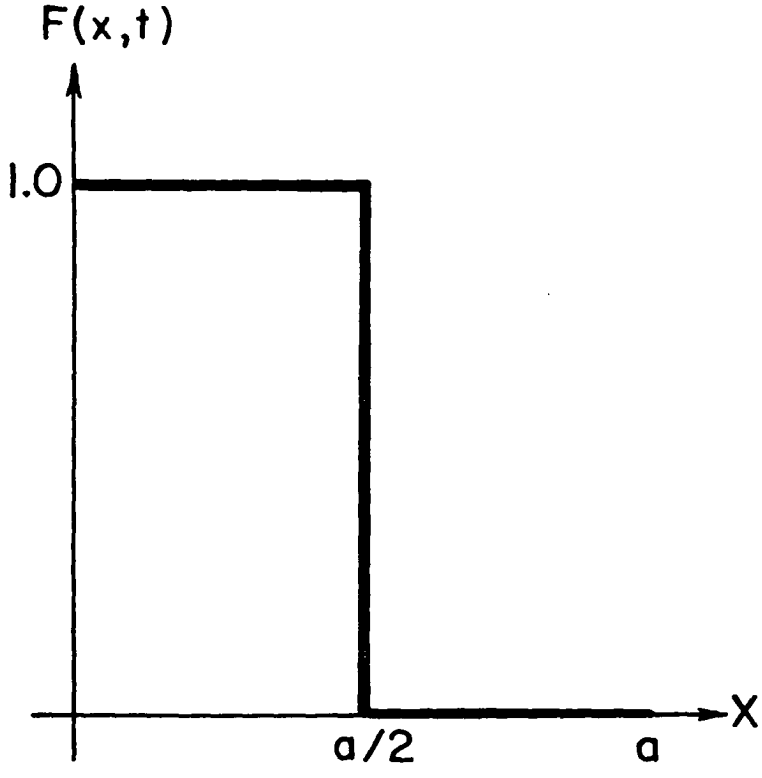
$$C = C_{RO} \text{ for } t = 0 \text{ at } a/2 < x < a \quad (32)$$

Since both ends are sealed, the boundary conditions are

Figure 12. Initial conditions (A) of C(x,t) and (B) of F(x,t)



A



B

$$\partial C/\partial x = 0 \text{ for all } t \text{ at } x = 0,\ x = a \qquad (33)$$

The calculation of the self-diffusion coefficient is simplified by letting

$$F(x,t) = \left[C(x,t) - C_{RO}\right]/(C_{LO} - C_{RO}) \qquad (34)$$

Then it is seen by differentiating equation 34 with respect to t that

$$(C_{LO} - C_{RO})(\partial F/\partial t) = (\partial C/\partial t) \qquad (35)$$

and differentiating equation 34 twice with respect to x and multiplying both sides by D_s then

$$D_s(C_{LO} - C_{RO})(\partial^2 F/\partial x^2) = D_s(\partial^2 C/\partial x^2) \qquad (36)$$

Now from equations 30, 35, and 36, one obtains

$$\partial F/\partial t = D_s(\partial^2 F/\partial x^2) \qquad (37)$$

After the transformation the initial conditions (see Figure 4B) for F(x,t) are, using equations 31 and 34

$$F = 1,\ t = 0,\ 0 < x < a/2$$

and using equations 32 and 34

$$F = 0,\ t = 0,\ a/2 < x < a$$

and from equations 33 and 34 the boundary conditions are

$$\partial F/\partial x = 0 \text{ for all } t \text{ at } x = 0,\ x = a$$

A solution of equation 37, as is evident from Crank (10, p. 16), is obtained by adding a needed constant.

$$F = B_0/2 + (A_n \sin\lambda x + B_n \cos\lambda x)e^{-\lambda^2 D_s t} \qquad (38)$$

By taking $\lambda = n\pi/a$ and letting $A_n = 0$ it is seen that the boundary condition is satisfied. Equation 38 then becomes

$$F = B_o/2 + \sum_{n=1}^{\infty} B_n \cos(n\pi x/a) e^{-D_s t(n\pi/a)^2}$$

yielding at t = 0

$$F_{t=0} = B_o/2 + \sum_{n=1}^{\infty} B_n \cos(n\pi x/a)$$

This is a half range Fourier cosine series for which the B_n will satisfy all initial conditions if

$$B_n = (2/a)\int_o^{a/2} \left[1 \cdot \cos(n\pi x/a)\right] dx$$

$$+(2/a)\int_{a/2}^{a} \left[0 \cdot \cos(n\pi x/a)\right] dx$$

$$= (2/n\pi) \sin(n\pi/2), \quad n = 1, 2, \ldots$$

$$B_o = 1$$

Under these conditions the solution of the differential equation, as given in Loeb (26) reduces to

$$F = 1/2 + (2/\pi)\sum_{n=1}^{\infty} (1/n)\sin(n\pi/a) \cdot \cos(n\pi x/a) e^{-D_s t(n\pi/a)^2} \qquad (39)$$

where

$F = (C - C_{RO})/(C_{LO} - C_{RO})$, $C \leq C_{LO}$

D_s = self-diffusion coefficient (cm.^{2}/sec.)

t = time (sec.)

a = total length of soil core (cm.)

The average concentration in the intervals 0 to a/2 and a/2

to a can be computed in terms of D_s and t from the series by the formulae

$$F_L = (2/a) \int_0^{a/2} F dx$$

$$F_R = (2/a) \int_{a/2}^{a} F dx$$

where F_L and F_R are the average value of F in the left and right side of the system, respectively. Upon integration the equations yield

$$F_L = 1/2 + (4/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \sin^2(n\pi/2) e^{-D_s t (n\pi/a)^2} \qquad (40)$$

$$F_R = 1/2 - (4/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \sin^2(n\pi/2) e^{-D_s t (n\pi/a)^2} \qquad (41)$$

For this experiment the contribution of terms after the first three was found to be insignificant. For longer intervals only one or two terms are necessary. The value of the self-diffusion coefficient is of primary interest. It is obtained by successive approximations or by graphical methods.

Experimental verification of the self-diffusion equation

Method Colo clay loam soil and 28-micron diameter glass beads were used in separate self-diffusion experiments. Weighed quantities of each of these materials were uniformly moistened to different moisture contents with a fine water

spray. In each case the medium was stirred periodically to assure the attaining of a predetermined moisture content. This moistening process was accomplished for two equal portions of each soil material, one with tagged water and one with resin-filtered tap water. The soil material containing the tagged and untagged soil moisture was then packed, as uniformly as possible, into two separate aluminum cylinders, 3 inches long and 3 inches in inside diameter. Two soil cores were thus formed, one tagged and one untagged. One end of the tagged core was pressed into close contact with an end of the untagged core. The outside of the joint where the aluminum cylinders made contact was sealed with scotch electrical tape. The remaining open ends were sealed with metal plates and paraffin. The cores, now fused, were placed in a horizontal position in a constant temperature environment of $25^{\circ} \pm 0.1^{\circ}$ C. This was accomplished by placing the samples in a water-tight container and submerging the container in a constant temperature bath.

The time that the cores were kept in the constant temperature environment varied for different experiments. The cores in these two experiments, one for the Colo clay loam soil and the other for the glass beads, were kept in the constant temperature environment for 57 and 97 hours, respectively. After this time the soil cores were sliced up into 14 sections of equal length (about 1 cm.). The moisture was extracted as

described in a previous section and analyzed for its D content.

In computing the self-diffusion coefficient, an average DOH concentration, as obtained from the D measurements of the water extracted from the seven segments of each half-core, was used. A procedure for converting average concentrations to self-diffusion coefficients is given by Obermayer (31). Obermayer combines equations 40 and 41 which results in

$$(F_L - F_R)/(F_L + F_R) = (8/\pi^2)\sum_{n=1}^{\infty}(1/n^2)e^{-D_s t(n\pi/a)^2} \quad (42)$$

$$n = 1, 3, 5, \ldots$$

F_L and F_R may be obtained by substituting actual D measurements into equation 34. In this equation C is the average of the seven measurements from each half-core, C_{LO} is the concentration of the tagged half-core at t = 0, and C_{RO} is the concentration of the untagged core at t = 0. Obermayer (31) has published a table for values of $D_s t$ corresponding to $(F_L - F_R)/(F_L + F_R)$. The exact values of $D_s t$ may be obtained from these tables by interpolation since the relationship of $D_s t$ and $(F_L - F_R)/(F_L + F_R)$ approaches linearity over small intervals of $D_s t$. Since Obermayer's value of "a" was different than the "a" used in this experiment, the value $D_s t$ was multiplied by $(a/a')^2$ where a' is Obermayer's value of 0.8662 meters. This table was found to be very useful in computing the self-diffusion coefficients.

With equation 42 available it is seen that the sectioning of the core and determining the D content of each of the seven sections of the half core are not necessary when computing only the self-diffusion coefficient. The sectioning was done to see how the tagged water distributed itself throughout the whole soil core, and how well the experimental data coincided with the values obtained from equation 39.

Results The measured DOH content of the soil moisture removed from the core segments of the Colo clay loam soil is shown in Table 3. The thickness of these soil segments is 1.09 cm. The percent moisture was found to be almost uniform. This was thus as it should be for the supposed experimental condition of uniform moisture content. The measured D values show that the tagged water has moved from the left half into the right half of the soil core and the untagged water has moved in the opposite direction.

By substituting the average of the seven experimentally determined values from each half-core into equation 42, the self-diffusion coefficient was determined. The self-diffusion coefficient for the Colo clay loam soil was 0.61×10^{-5} $cm.^2/sec$. The values for $D_s(0.61 \times 10^{-5})$ and t (57 hours) were substituted into equation 39 to see how well the theory checked with the actual distribution of DOH in the soil core. A comparison of theory with the experimental data for the Colo loam soil is shown in Figure 13.

Table 3. Distribution of total and tagged water in the Colo clay loam soil core after 57 hours

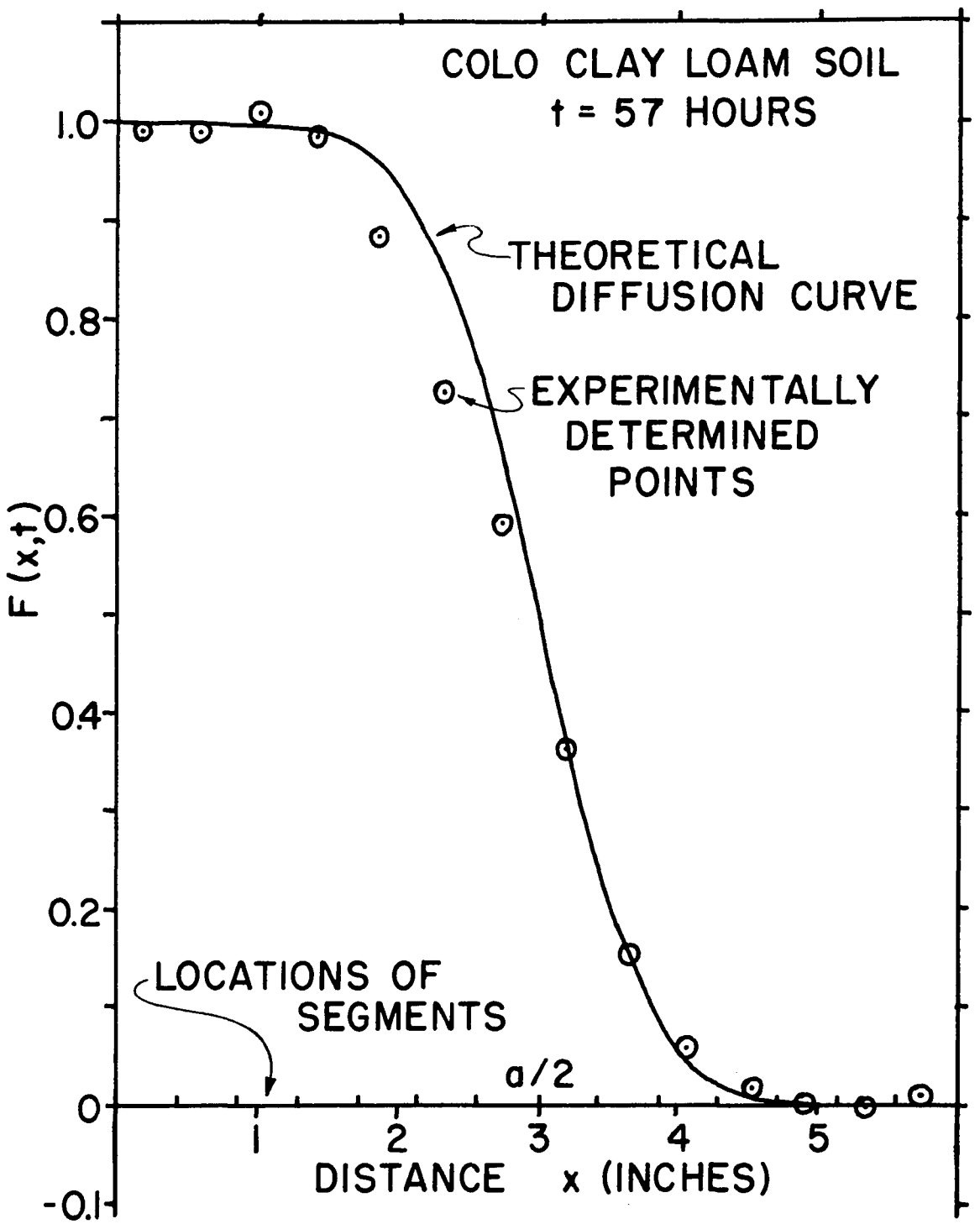
Segments in soil core	Distance from left side cm.	Moisture content %[a]	Measured D content ppm.[b]	F(x,t)[c]
Left half of soil core				
1	.55	37.02	2582	0.995
2	1.64	36.40	2576	0.993
3	2.73	35.80	2624	1.012
4	3.82	36.09	2563	0.987
5	5.91	36.40	2311	0.884
6	6.00	37.06	1923	0.725
7	7.09	37.65	1596	0.592
Right half of soil core				
8	8.18	37.84	1065	0.374
9	9.27	37.57	542	0.160
10	10.36	36.87	287	0.056
11	11.45	37.74	189	0.016
12	12.54	37.40	155	0.002
13	13.63	37.54	140	-0.004
14	14.72	37.96	169	0.008

[a]Oven-dry basis

[b]Parts of D per million parts of (D + H).

[c]Distribution function; see text, equations 34 and 39.

Figure 13. Experimental values for a moist clay loam soil and theoretical values of $F(x,t)$ of equation 39 versus x for t = 57 hours and D_s = 0.61 $cm.^2/sec.$


COLO CLAY LOAM SOIL
t = 57 HOURS
THEORETICAL
DIFFUSION CURVE
EXPERIMENTALLY
DETERMINED
POINTS
LOCATIONS OF
SEGMENTS
a/2
F (x,t)
1.0
0.8
0.6
0.4
0.2
0
-0.1
1
2
3
4
5
DISTANCE x (INCHES)

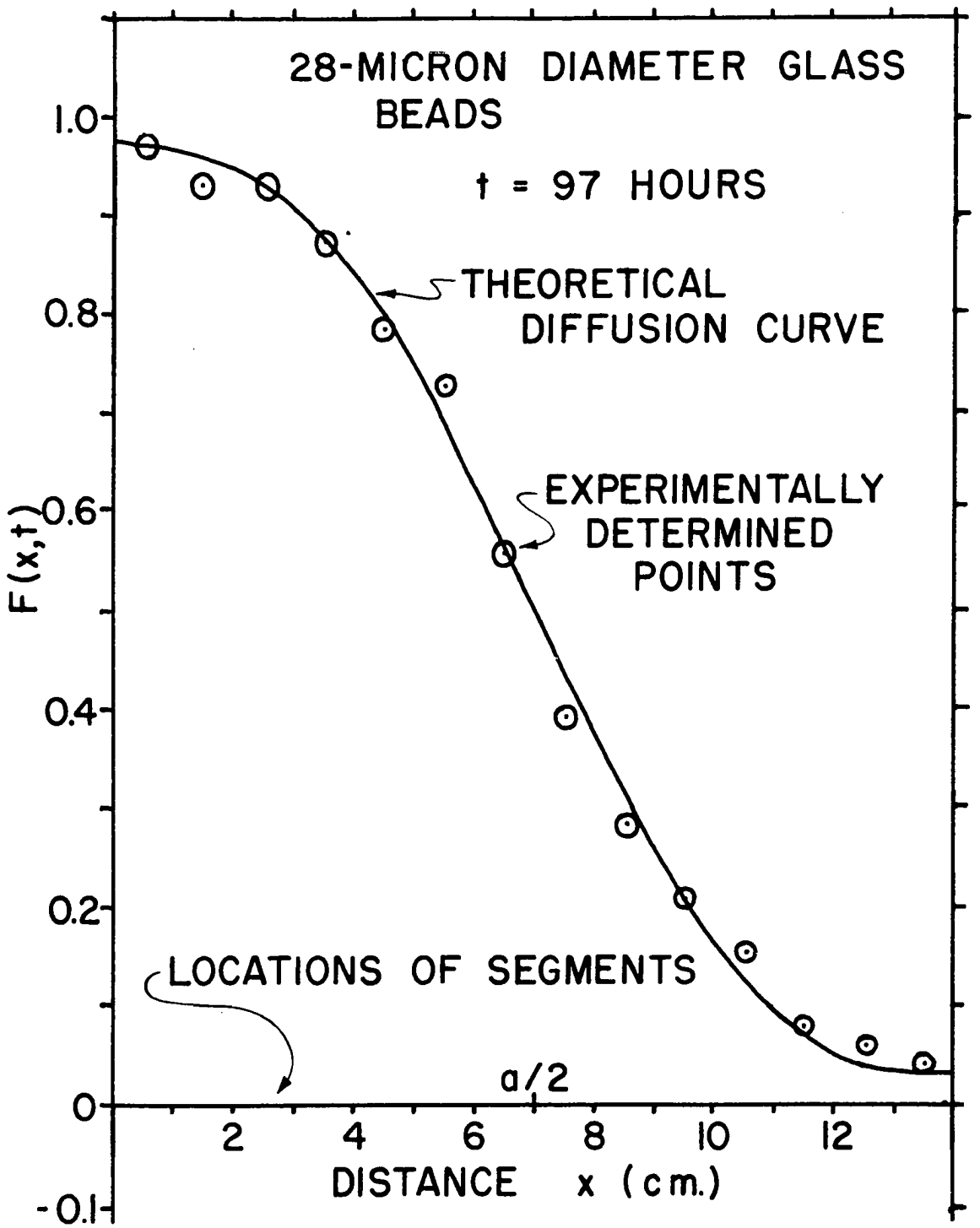
Physical properties of the Colo clay loam soil core which was analyzed in detail were as follows: bulk density, 1.25 gm./cc; average moisture percent by volume, 27.5 percent; air-filled pore space, 20 percent; and approximate moisture tension, 20 cm.

The same type of detailed analysis was conducted with a core of 28 micron diameter glass beads. Here the core was sectioned into 14 segments, each of one cm. length. The magnitude of the self-diffusion coefficient was 1.36×10^{-5} $cm.^2/sec$. This value and 97 hours for t were substituted into equation 39. A comparison of theory with the experimental data for the glass beads is shown in Figure 14.

Physical properties of the core of 28-micron diameter glass beads which was analyzed in detail were as follows: bulk density, 1.25 grams/cc.; average moisture percent by volume, 27.5 percent; air-filled pore space, 20 percent; and approximate moisture tension, 20 cm.

Discussion The variation encountered between experimental measurements and theory is relatively small as shown in Figures 13 and 14. The data also indicate that Ds, the self-diffusion coefficient, is a constant as assumed in equation 30 and that the linear diffusion law and the theory as a whole are therefore valid for this experimental technique. If the data had not coincided between theory and experiment, the equation used in determining the self-diffusion coeffi-

Figure 14. Experimental values for moist glass beads and theoretical values of $F(x,t)$ of equation 39 versus x for t = 97 hours and D_s = 1.36 $cm.^2/sec.$


28-MICRON DIAMETER GLASS BEADS
t = 97 HOURS
THEORETICAL DIFFUSION CURVE
EXPERIMENTALLY DETERMINED POINTS
LOCATIONS OF SEGMENTS
a/2
F(x,t)
1.0
0.8
0.6
0.4
0.2
0
-0.1
2
4
6
8
10
12
DISTANCE x (cm.)

cient may not have been applicable. Two factors contribute to the validity of the experiments: 1) very small concentrations of DOH were used so that a self-diffusion coefficient of essentially pure HOH was in question, and 2) the difference in mass between HOH and DOH is relatively small, making those DOH molecules used essentially like the HOH molecules. The deviations from theory of segments 5 and 6 in Figure 13 are not the result of errors in measurement by the mass spectrometer. With the gradient of $F(x,t)$ as sharp as it was, the errors were probably due to errors in measuring the lengths of the soil core segments. Non-uniformity in packing of the soil and consequently the moisture content could also have contributed to the deviation from the expected value. Still another source of error causing the deviation of points from the theoretical curve could have been a picking-up of water vapor from the atmosphere or a loss of water vapor to the atmosphere while the sectioning technique was performed. A much better fit was obtained between theoretical and experimental values in the case of the glass beads (Figure 14). This is probably due to the greater homogeneity of the material.

For the glass bead experiment the time period was nearly twice that used in the Colo clay loam soil experiment. There is reason to believe that the time factor will not present any problems if the average DOH concentrations of each half of

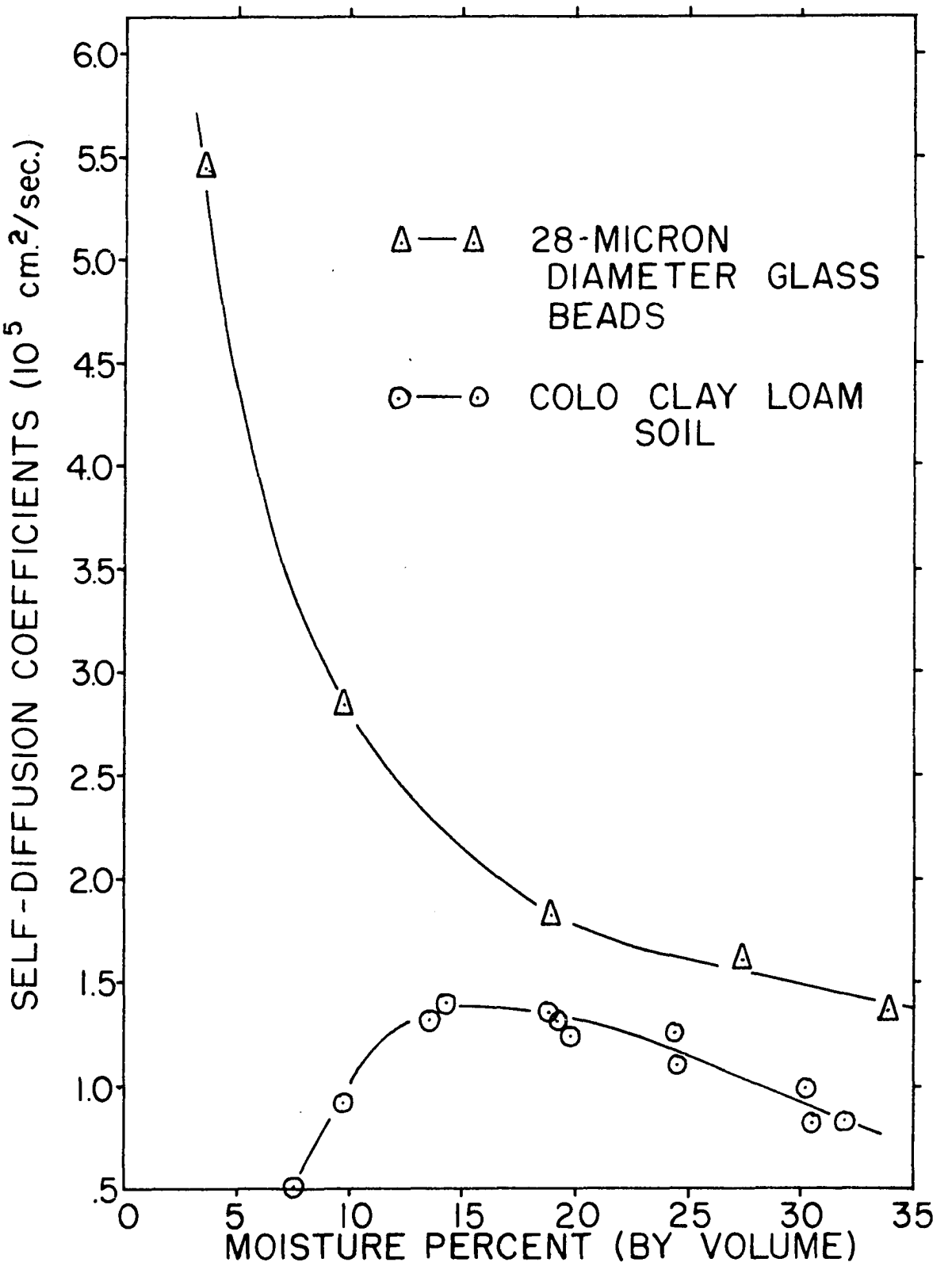
the core are sufficiently different. Periods of up to 200 hours have been used with some experiments. The magnitude of these self-diffusion coefficients was, within experimental error, the same as those obtained for shorter periods of time.

Further self-diffusion measurements

Method The self-diffusion measurement technique described in previous sections is not very suitable for a series of self-diffusion measurements. It has served to verify the basic theory. Equation 42 is also a suitable equation for general work and it is used in the following. To use this equation it is required only to take a representative deuterium sample from the whole length of each half-core. A 3/4-inch cork-borer was found to be an excellent tool for taking such soil samples. The whole half-core itself could have served as a sample, but because of its large volume, the extraction of a representative tagged water sample could not be readily accomplished.

Results The self-diffusion coefficients of 12 cores of Colo clay loam soil and five cores of 28-micron diameter glass beads were determined. Physical properties of these cores are shown in Appendix A and the necessary values for computing self-diffusion coefficients are shown in Appendix B. The relationship between the self-diffusion coefficients and moisture content is shown in Figure 15. The self-diffusion experiments for Colo clay loam soil were replicated. Deviations

Figure 15. Self-diffusion coefficients of water in Colo clay loam soil and 28-micron diameter glass beads plotted as a function of the moisture percent by volume


SELF-DIFFUSION COEFFICIENTS (10^5 cm.^{2}/sec.)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0
5
10
15
20
25
30
35
MOISTURE PERCENT (BY VOLUME)
Δ—Δ 28-MICRON DIAMETER GLASS BEADS
⊙—⊙ COLO CLAY LOAM SOIL

of the experimental points from the smooth curves shown are probably a consequence largely of differences in soil core densities.

Discussion At the present state of knowledge the self-diffusion coefficient moisture curves shown in Figure 15 cannot be explained. Since normal soil moisture diffusion, as defined by Philip (34), occurs in the liquid, vapor and adsorbed phases, self-diffusion undoubtedly occurs in these same phases. Diffusion in the adsorbed phase was considered by de Boer (12, p. 226) to be a diffusion through surface migration. With the 28-micron diameter glass beads the surface area is small and self-diffusion in the adsorbed phase should be negligible.

At the highest water content (34 percent) at which only 5 percent air-filled pore space exists, a self-diffusion coefficient of 1.36×10^{-5} cm./sec. was obtained. Wang et al. (46) obtained a self-diffusion coefficient of 2.34×10^{-5} $cm.^2/sec.$ for pure water at the same temperature (25° C.). Whether the difference between these two self-diffusion values may be attributed entirely to the soil matrix, per se, is not known. It would appear that the magnitude of the self-diffusion coefficient in the liquid phase would not be influenced much by the tortuosity factor because of the short diffusion path of the water molecules when in this phase.

The adsorptive forces of the soil particles which reduce

the molecular activity of the water may also be responsible for the observed reduction in the magnitude of the self-diffusion coefficient. This is obvious if one compares the glass bead self-diffusion values with those for Colo clay loam soil, the combined adsorptive forces being much greater in the latter.

Throughout the intermediate moisture range one will have to consider tagged water molecules moving through liquid and vapor islands as pointed out by Philip and de Vries (36). Self-diffusion in the liquid phase will continue piecewise as long as some continuity of the moisture films persists. Self-diffusion in the vapor phase will continue as long as any water vapor remains in the soil.

If one plots the self-diffusion coefficients of Figures 13 and 14 on the graphs of Figure 15, they depart from the curves more than do the other points. These departures may be a consequence of moisture exchange with the atmosphere when the sectioning process was used, or it may be a consequence of the seven core sections not having given as true an average of the deuterium distribution as single representative continuous core samples. There may have been other reasons.

Proposed Future Work for Soil Experiments

Although no relationship has been established between the self-diffusion coefficient of water and the moisture gradient

diffusion coefficient, yet both coefficients are largely the result of the thermal energy of the water molecules. Philip (35) believes that there are no simple relationships between the osmotic diffusion coefficient and the self-diffusion coefficient. Apparently the same holds true for the purely hydrological relationships, namely $K(\partial\psi/\partial\theta) = D$ as defined by Philip (34), and D_s.

Even though one can not as yet relate the diffusion coefficients mentioned above to self-diffusion coefficients, the studies of self-diffusion of soil water have interesting aspects. A good example where a knowledge of self-diffusion is important might be the study of a saturated flow problem or other type flow problem where the mass movement of water from a specific location is measured by using tagged water molecules. Unless the mass movement is very large in relation to the self-diffusion, considerable difficulty would be experienced in determining the actual mass movement unless self-diffusion were accounted for. The need to account for self-diffusion was clearly shown in the first soil experiment. If an investigator has a better understanding of the self-diffusion phenomenon, he may conduct his experiment under conditions so as to minimize this effect when it is interfering.

Another area of interest in this field may be in the study of nitrate movement or other water-soluble ions in soil

water. Also the movement of dissolved gases, such as oxygen, in soil moisture may still be another area of interest connected with the self-diffusion phenomenon. To soil water, in its own realm, studies of self-diffusion should be of academic interest because the self-diffusion coefficient is a measure of response of water molecules to a particular environment. With respect to the importance of the evaporation and transpiration processes in our whole water economy, further work in this field should be rewarding.

Conclusions of Soil Experiments

1. DOH was found to have a limited use in tracing mass flow of water under unsaturated conditions because of the magnitude of the self-diffusion effect.

2. A theoretical self-diffusion equation was derived and experimentally verified for a soil system.

3. The magnitudes of self-diffusion coefficients between 28-micron diameter glass beads and Colo clay loam soil were found to be vastly different, especially at lower moisture contents.

4. Self-diffusion appears to be based on some of the physical laws governing normal soil moisture diffusion; however no basic relationship between normal soil moisture diffusion and self-diffusion could be established.

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APPENDIX A

Table 4. Physical measurements of laboratory prepared cores of Colo clay loam soil and 28-micron diameter glass beads

Sample number[b]	Moisture content (% by vol.)	Density (gms./cm.3)	Total porosity[a] (% by vol.)	Free air space (% by vol.)
1a	32.67	1.20	54.7	22.0
1b	32.00	1.23	43.6	21.6
2a	29.66	1.03	61.1	29.1
2b	30.66	1.05	60.4	29.7
3a	30.32	1.09	58.9	28.6
3b	30.99	1.09	58.9	27.9
4a	24.33	1.02	61.5	37.2
4b	24.33	1.03	61.1	36.8
5a	24.66	1.10	58.5	33.8
5b	25.01	1.11	58.1	33.1
6a	18.33	1.05	60.4	42.1
6b	19.66	1.06	60.0	40.3
7a	19.00	1.06	60.0	41.0
7b	20.00	1.04	60.6	40.6

[a]Values are based on a specific gravity value of 2.65 for Colo clay loam soil and of 2.39 for the 28-micron glass beads.

[b]Sample numbers 1-12 are for samples of Colo clay loam soil; sample numbers 13-17 are for samples of 28-micron glass beads.

Table 4. (Continued)

Sample number	Moisture content (% by vol.)	Density ($gms./cm.^3$)	Total porosity (% by vol.)	Free air space (% by vol.)
8a	18.67	1.10	58.5	39.8
8b	19.67	1.10	58.5	38.8
9a	14.33	1.14	57.0	42.7
9b	14.00	1.12	57.8	43.8
10a	13.29	1.09	58.9	45.6
10b	13.00	1.11	58.1	45.1
11a	9.69	1.10	58.5	48.8
11b	11.00	1.10	58.5	47.5
12a	7.58	1.08	59.2	51.6
12b	7.67	1.05	60.4	52.7
13a	34.67	1.45	39.3	4.6
13b	33.00	1.43	41.2	8.2
14a	27.50	1.25	47.7	20.2
14b	27.50	1.25	47.7	20.2
15a	18.66	1.25	47.7	29.0
15b	18.66	1.25	47.7	29.0
16a	9.67	1.23	48.5	38.8
16b	9.67	1.25	47.7	38.0
17a	4.00	1.24	48.1	44.1
17b	3.36	1.24	48.1	44.7

APPENDIX B

Table 5. Concentrations of D in soil moisture samples as determined with the mass spectrometer; and values of the self-diffusion coefficient as determined from the D concentrations with the use of equation 39

Sample number[a]	Time hrs.	C_{LO} ppm.	C_{RO} ppm.	C_L ppm.	C_R ppm.	F_L	F_R[b]	$\frac{F_L - F_R}{F_L + F_R}$	D_s[c]
1	200	2295	150	1776	555	0.7580	0.1881	0.6013	0.850
2	202	2269	150	1813	619	0.7885	0.2213	0.5617	1.017
3	100	2268	150	1973	--	0.8607	0.1397	0.7210	0.832
4	202	2126	150	1628	632	0.7479	0.2439	0.5081	1.283
5	100	2116	150	1800	--	0.8393	0.1607	0.6786	1.104
6	200	1984	150	1477	601	0.7235	0.2459	0.4926	1.379
7	216	2064	150	1568	625	0.7408	0.2481	0.4982	1.249
8	100	2046	150	1712	--	0.8238	0.1762	0.6476	1.328
9	200	2045	150	1575	644	0.7519	0.2606	0.4851	1.421
10	100	2047	150	1711	--	0.8229	0.1771	0.6458	1.342
11	96	1801	150	1564	--	0.8564	0.1436	0.7128	0.915
12	96	1554	150	1405	--	0.8939	0.1061	0.7878	0.501
13	95	2018	150	1723	485	0.8421	0.1793	0.6489	1.388
14	97	2013	150	1686	513	0.8245	0.1948	0.6178	1.618
15	129	1748	150	1422	540	0.7960	0.2440	0.5307	1.827
16	97	1889	150	1421	582	0.7308	0.2484	0.4926	2.843
17	100	1761	150	1273	747	0.6971	0.3706	0.3058	5.449

[a]Sample numbers 1-12 are for samples of Colo clay loam soil; sample number 13-17 are for samples of 28-micron beads.

[b]When C_R was not measured, values of F_R were obtained by subtraction $(1 - F_L)$.

[c]Values of D_s are given in 10^5 cm.^{2}/sec.